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OF THE

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**THE ASSOCIATION OF OFFICIAL AGRICULTURAL CHEMISTS**

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# PROCEEDINGS OF THE FORTY-NINTH ANNUAL CONVENTION OF THE ASSOCIATION OF OFFICIAL AGRICULTURAL CHEMISTS, 1933

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The forty-ninth annual convention of the Association of Official Agricultural Chemists was held at the Raleigh Hotel, Washington D.C., November 6-8, 1933.

The meeting was called to order by the president, James W. Kellogg, Department of Agriculture, Harrisburg, Pa., on the morning of November 6, at 10:30 o'clock.

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## OFFICERS, COMMITTEES, REFEREES, AND ASSOCIATE REFEREES OF THE ASSOCIATION OF OFFICIAL AGRICULTURAL CHEMISTS FOR THE YEAR ENDING NOVEMBER, 1934

### *President*

R. HARCOURT, Ontario Agricultural College, Guelph, Canada

### *Vice-President*

F. C. BLANCK, Washington, D.C.

### *Secretary-Treasurer*

W. W. SKINNER, Bureau of Chemistry and Soils, Washington, D.C.

### *Additional Members of the Executive Committee*

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C. C. McDONNELL, Washington, D.C.

H. R. KRAYBILL, Lafayette, Ind.

J. W. KELLOGG, Harrisburg, Pa.

### PERMANENT COMMITTEES

#### *Recommendations of Referees*

(Figures in parentheses refer to year in which appointment expires.)

E. M. BAILEY (Agricultural Experiment Station, New Haven, Conn.), *Chairman*

SUBCOMMITTEE A: H. H. HANSON (1934), (State Board of Agriculture, Dover, Del.), *Chairman*; H. R. Kraybill (1936); G. L. Bidwell (1938). [Insecticides, fungicides, and caustic poisons (fluorine compounds); soils and liming materials (hydrogen-ion concentration, alkaline soils and acid soils; liming materials, less common metals in soils); feeding stuffs (stock feed adulteration, mineral mixed feeds, moisture, hydrocyanic acid in glucoside-bearing materials, solvents for determination of fat, biological methods for determination of cod-liver oil in feed mixtures, fat in dairy products used as feeds, preparation of solution and determination of sugar, biological methods for vitamin B com-



plexes, technic and details in biological methods vitamin D carriers, mechanical classification of alfalfa products, fluorine, qualitative tests for proteins); sugars and sugar products (honey, maple products; drying, densimetric, and refractometric methods; polariscopic methods, chemical methods for reducing sugars, lead precipitate); fertilizers (phosphoric acid, nitrogen, high analysis fertilizers, potash); plants (less common metals, total chlorine, carbohydrates, forms of nitrogen, sodium and potassium); lignin, enzymes, paints; waters, brine and salt.]

**SUBCOMMITTEE B:** A. G. Murray (1934), (U. S. Food and Drug Administration, Washington, D. C.), *Chairman*; L. E. Warren (1936); L. B. Broughton (1938). [Naval stores (resin, turpentine); drugs (crude drugs, radioactivity in foods and drugs, mercurials, microchemical methods for alkaloids, hypophosphites, santonin, ether, benzyl compounds, small quantities of morphine in sirups, guaiacol; rhubarb and rhaponticum, tetrachlorethylene, hexylresorcinol, ergot alkaloids, microchemical methods for synthetics, nitrites in tablets, ointments, biological testing, acetphenetidin in presence of caffeine and aspirin, resins and oleoresins, pyridium, gums, essential oils, psyllium seed); beers, wines, and distilled liquors.]

**SUBCOMMITTEE C:** G. G. Frary (1934), (Department of Agriculture, Vermilion, S. D.), *Chairman*; H. A. Lepper (1936); J. O. Clarke (1938). [Dairy products (butter, cheese, malted milk, dried milk, ice cream and gelatin, milk proteins, lactose); oils, fats and waxes (refractometric methods for oil in seeds, hydroxyl number and acetyl value, aldehyde-free alcohol); eggs and egg products (reducing sugars, sucrose, added salt, fat, lipoids,  $P_2O_5$  and crude albumin nitrogen; detection of decomposition, glycerol and unsaponifiable matter); food preservatives; coloring matters in foods; metals in foods (arsenic, copper and zinc, fluorine, lead); fruits and fruit products (soluble solids and effect of acids on sugar on drying, pectic acid and electrolytic titration acidity, fruit acids, moisture in dried fruits); canned foods, vinegars; flavors and non-alcoholic beverages; meats and meat products; gelatin; cacao products (milk solids in milk cacao products, shell in cacao products); gums in foods, spices; baking powders and baking chemicals; cereal foods (ash in flour, macaroni products and baked products; chlorides in flour and baked products, and moisture in baked products containing fruit; H-ion concentration of flour, diastatic value of flour, starch in flour, flour-bleaching chemicals, foreign methods for testing flour,  $CO_2$  in self-rising flour, methods for macaroni products, bread and baked products; (a) unsaponifiable matter, (b) fat, crude albumin nitrogen, lipoid  $P_2O_5$ , (c) crude fiber in baked products; milk solids in milk bread, rye in flour mixtures, viscosity of flour, cold water extract flour, ergot in flour, catalase and proteolytic enzymes, color in flour); microchemical methods, microbiological methods—canned foods (treatment of unopened container, sampling inoculum, culture media of non-acid products, culture media of acid products, incubation periods and temperature for cultures); nuts and nut products.]

*Committee to Cooperate with Other Committees on Food Definitions*

C. D. HOWARD (Board of Health, Concord, N. H.), *Chairman*

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G. G. FRARY

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*Principles and Practice of Agricultural Analysis*

C. A. BROWNE and W. W. SKINNER (Bureau of Chemistry and  
 Soils, Washington, D. C.)

## SPECIAL COMMITTEES

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A. G. MCCALL, *Soils and Liming Materials*; C. C. McDONNELL, *Insecticides*

*and Fungicides*; L. E. BOPST, *Fertilizers*; F. W. ZERBAN, *Sacharine Products*;

R. W. FREY, *Tanning Materials and Leathers*; J. W. SALE, *Water*; O. B. WINTER,

*Plants.*

**REFEREES AND ASSOCIATE REFEREES**

**INSECTICIDES, FUNGICIDES, AND CAUSTIC POISONS**

*General referee:* J. J. T. Graham, Food and Drug Adm., Washington, D. C.

**FLUORINE COMPOUNDS:**

*Associate referee:* G. A. Shuey, Agricultural Experiment Station, Knoxville, Tenn.

**SOILS AND LIMING MATERIALS:**

*General referee:* W. H. MacIntire, Agricultural Experiment Station, Knoxville, Tenn.

**HYDROGEN-ION CONCENTRATION**

**a. ALKALINE SOILS:**

*Associate referee:* P. L. Hibbard, University of California, Berkeley, Calif.

**b. ACID SOILS:**

*Associate referee:* M. F. Morgan, Agricultural Experiment Station, New Haven, Conn.

**LIMING MATERIALS:**

*Associate referee:* W. M. Shaw, Agricultural Experiment Station, Knoxville, Tenn.

**LESS COMMON METALS IN SOILS:**

*Associate referee:* J. S. McHargue, Agricultural Experiment Station, Lexington, Ky.

**FEEDING STUFFS:**

*General referee:* V. E. Munsey, Food and Drug Adm., Washington, D. C.

**STOCK FEED ADULTERATION:**

*Associate referee:* H. R. Walls, College Park, Md.

**MINERAL MIXED FEEDS:**

*Associate referee:* H. A. Halvorson, Old Capitol Building, St. Paul, Minn.

**MOISTURE:**

*Associate referee:* G. E. Grattan, Department of Agriculture, Ottawa, Canada

**HYDROCYANIC ACID IN GLUCOSE-BEARING MATERIALS:**

*Associate referee:* G. C. Smith, Food and Drug Adm., Washington, D. C.

**SOLVENTS FOR DETERMINATION OF FAT IN FEEDING STUFFS:**

*Associate referee:* L. S. Walker, Agricultural Experiment Station, Burlington, Vt.

**BIOLOGICAL METHODS FOR DETERMINATION OF COD LIVER OIL IN FEED MIXTURES:**

*Associate referee:* W. B. Griem, Department of Agriculture and Markets, Madison, Wis.

**FAT IN DAIRY PRODUCTS USED AS FEEDS:**

*Associate referee:* W. Catesby Jones, Department of Agriculture, Richmond, Va.

**PREPARATION OF SOLUTION AND DETERMINATION OF SUGAR:**

*Associate referee:* J. B. Snider, Food and Drug Adm., Savannah, Ga.

**BIOLOGICAL METHODS FOR VITAMIN B COMPLEXES:**

*Associate referee:* C. A. Elvehjem, Dept. of Agricultural Chemistry, Madison, Wis.

**TECHNIC AND DETAILS OF BIOLOGICAL METHODS, VITAMIN D CARRIERS:**

*Associate referee:* L. L. Latchat, Dept. of Agriculture Dairy and Food, St. Paul, Minn.

**MECHANICAL CLASSIFICATION OF ALFALFA PRODUCTS:**

*Associate referee:* W. L. Hall, Bureau of Agricultural Economics, Washington, D.C.

**QUALITATIVE TESTS FOR PROTEINS:**

*Associate referee:* D. Breese Jones, Bureau of Chemistry and Soils, Washington, D.C.

**SUGARS AND SUGAR PRODUCTS:**

*General referee:* C. A. Browne, Bureau of Chemistry and Soils, Washington, D. C.

**HONEY:**

*Associate referee:* H. A. Schuette University of Wisconsin, Madison, Wis.

**MAPLE PRODUCTS:**

*Associate referee:* J. F. Snell, Macdonald College, Quebec, Canada.

**DRYING, DENSIMETRIC, AND REFRACTOMETRIC METHODS:**

*Associate referee:* C. F. Snyder, Bureau of Standards, Washington, D. C.

**POLARISCOPIC METHODS:**

*Associate referee:* S. Byall, Bureau of Chemistry and Soils, Washington, D. C.

**CHEMICAL METHODS FOR REDUCING SUGARS:**

*Associate referee:* R. F. Jackson, Bureau of Standards, Washington, D. C.

**LEAD PRECIPITATE:**

*Associate referee:* F. W. Zerban, N. Y. Sugar Trade Lab., New York City

**FERTILIZERS:**

*General referee:* G. S. Fraps, Agricultural Experiment Station, College Station, Tex.

**PHOSPHORIC ACID:**

*Associate referee:* W. H. Ross, Bureau of Chemistry and Soils, Washington, D. C.

**NITROGEN:**

*Associate referee:* A. L. Prince, Agricultural Experiment Station, New Brunswick, N. J.

**HIGH ANALYSIS FERTILIZERS:**

*Associate referee:* J. B. Smith, Agricultural Experiment Station, Kingston, R. I.

POTASH:

*Associate referee:* H. R. Kraybill, Agricultural Experiment Station, Lafayette, Ind.

PLANTS:

*General referee:* O. B. Winter, Agricultural Experiment Station, E. Lansing, Mich.

LESS COMMON METALS:

*Associate referee:* J. S. McHargue, Agricultural Experiment Station, Lexington, Ky.

TOTAL CHLORINE:

*Associate referee:* H. L. Wilkins, Bureau of Plant Industry, Washington, D. C.

CARBOHYDRATES:

*Associate referee:* J. T. Sullivan, Agricultural Experiment Station, Lafayette, Ind.

FORMS OF NITROGEN:

*Associate referee:* H. B. Vickery, Agricultural Experiment Station, New Haven, Conn.

SODIUM AND POTASSIUM:

*Associate referee:* Lillian Butler, Agricultural Experiment Station, E. Lansing, Mich.

LIGNIN:

*General referee:* M. Philips, Bureau of Chemistry and Soils, Washington, D. C.

ENZYMES:

*General referee:* A. K. Balls, Bureau of Chemistry and Soils, Washington, D. C.

PAINTS, PAINT MATERIALS AND VARNISHES:

*General referee:* C. S. Ladd, Food Commissioner and Chemist, Bismarck, N.D.

PAPER AND PAPER MATERIALS:

*General referee:* T. D. Jarrell, Bureau of Chemistry and Soils, Washington, D. C.

WATERS, BRINE AND SALT:

*General referee:* C. H. Badger, Food and Drug Adm., Washington, D. C.

NAVAL STORES:

*General referee and associate referee on rosin:* F. P. Veitch, Bureau of Chemistry and Soils, Washington, D. C.

TURPENTINE:

*Associate referee:* V. E. Grotlisch, Food and Drug Adm., Washington, D. C.

DRUGS:

*General referee:* A. E. Paul, 1625 Transportation Bldg., Chicago, Ill.

**CRUDE DRUGS:**

*Associate referee:* H. W. Youngken, Massachusetts College of Pharmacy, Boston, Mass.

**RADIOACTIVITY IN FOODS AND DRUGS:**

*Associate referee:* C. H. Badger, Food and Drug Adm., Washington, D. C.

**MERCURIALS:**

*Associate referee:* E. C. Deal, Food and Drug Adm., New Orleans, La.

**MICROCHEMICAL METHODS FOR ALKALOIDS:**

*Associate referee:* C. K. Glycart, Food and Drug Adm., Chicago, Ill.

**MICROCHEMICAL METHODS FOR SYNTHETICS:**

*Associate referee:* I. S. Shupe, Food and Drug Adm., Chicago, Ill.

**HYPOPHOSPHITES:**

*Associate referee:* H. R. Bond, Food and Drug Adm., Chicago, Ill.

**SANTONIN:**

*Associate referee:* H. J. Fisher, Agricultural Experiment Station, New Haven, Conn.

**ETHER:**

*Associate referee:* W. F. Kunke, Food and Drug Adm., Chicago, Ill.

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*Associate referee:* J. Callaway, Jr., Food and Drug Adm., New York City

**TETRACHLORETHYLENE:**

*Associate referee:* G. M. Johnson, Food and Drug Adm., Chicago, Ill.

**SMALL QUANTITIES OF MORPHINE IN SIRUPS:**

*Associate referee:* E. O. Eaton, Food and Drug Adm., San Francisco, Calif.

**HEXYLRESORCINOL:**

*Associate referee:* J. Carol, Food and Drug Adm., Chicago, Ill.

**ERGOT ALKALOIDS:**

*Associate referee:* C. K. Glycart, Food and Drug Adm., Chicago, Ill.

**GUAIACOL:**

*Associate referee:* H. Wales, Food and Drug Adm., Washington, D. C.

**RHUBARB AND RHAPONTICUM:**

*Associate referee:* A. Viehoveer, Philadelphia College of Pharmacy, Philadelphia, Pa.

**BIOLOGICAL TESTING:**

*Associate referee:* W. T. McClosky, Food and Drug Adm., Washington, D. C.

**NITRITES IN TABLETS:**

*Associate referee:* F. C. Sinton, Food and Drug Adm., New York City

OINTMENTS:

*Associate referee:* W. F. Reindollar, State Dept. of Health, Baltimore, Md.

ACETPHENETIDIN IN PRESENCE OF CAFFEINE AND ASPIRIN:

*Associate referee:* L. E. Warren, Food and Drug Adm., Washington, D. C.

RESINS AND OLEORESINS:

*Associate referee:* L. E. Warren.

PYRIDIDIUM:

*Associate referee:* C. L. Clay, Dept. of Health, New Orleans, La.

GUMS:

*Associate referee:* J. H. Cannon, Food and Drug Adm., Chicago, Ill.

ESSENTIAL OILS:

*Associate referee:* Earl A. Anderson, Food and Drug Adm., New York City.

PSYLLIUM SEED:

*Associate referee:* H. M. Burlage, University of North Carolina, Chapel Hill, N. C.

DAIRY PRODUCTS:

*General referee:* G. G. Frary, Dairy and Food Dept., Vermilion, S. D.

BUTTER:

*Associate referee:* C. W. Harrison, Food and Drug Adm., Minneapolis, Minn.

CHEESE:

*Associate referee:* C. B. Stone, Food and Drug Adm., Minneapolis, Minn.

MALTED MILK:

*Associate referee:* F. Hillig, Food and Drug Adm., Washington, D. C.

DRIED MILK:

*Associate referee:* Leslie Hart, Food and Drug Adm., Washington, D. C.

ICE CREAM AND GELATIN:

*Associate referee:* G. G. Frary.

MILK PROTEINS:

*Associate referee:* G. P. Sanders, Bureau of Dairy Industry, Washington, D. C.

LACTOSE IN MILK:

*Associate referee:* E. R. Garrison, University of Missouri, Columbia, Mo.

OILS, FATS AND WAXES:

*General referee:* G. S. Jamieson, Bureau of Chemistry and Soils, Washington, D. C.

REFRACTOMETRIC DETERMINATION OF OIL IN SEEDS:

*Associate referee:* T. H. Hopper, Agricultural Experiment Station, Fargo, N. Dak.

**HYDROXYL NUMBER AND ACETYL VALUE:**

*Associate referee:* W. H. Roberts, Office of Food Commissioner and Chemist, Bismarck, N. D.

**ALDEHYDE-FREE ALCOHOL:**

*Associate referee:* G. S. Jamieson

**EGGS AND EGG PRODUCTS:**

*General referee:* H. A. Lepper, Food and Drug Adm., Washington, D. C.

**REDUCING SUGARS, SUCROSE, ADDED SALT, FAT, LIPOIDS,  $P_2O_5$ , AND CRUDE ALBUMIN NITROGEN:**

*Associate referee:* F. L. Hart, Food and Drug Adm., Washington, D. C.

**GLYCEROL AND UNSAPONIFIABLE MATTER:**

*Associate referee:* H. A. Lepper.

**DETECTION OF DECOMPOSITION:**

*Associate referee:* H. D. Grigsby, Food and Drug Adm., New York City.

**FOOD PRESERVATIVES:**

*General referee:* J. C. Krantz, Jr., State Department of Health, Baltimore, Md.

**COLORING MATTERS IN FOODS:**

*General referee:* C. F. Jablonski, Food and Drug Adm., New York City.

**METALS IN FOODS:**

*General referee:* H. J. Wichmann, Food and Drug Adm., Washington, D. C.

**ARSENIC:**

*Associate referee:* C. R. Gross, Bureau of Chemistry and Soils, Washington, D. C.

**COPPER AND ZINC:**

*Associate referee:* R. M. Mehurin, Bureau of Animal Industry, Washington, D. C.

**FLUORINE:**

*Associate referee:* Dan Dahle, Food and Drug Adm., Washington, D. C.

**LEAD:**

*Associate referee:* H. J. Wichmann.

**FRUITS AND FRUIT PRODUCTS:**

*General referee:* B. G. Hartmann, Food and Drug Adm., Washington, D. C.

**SOLUBLE SOLIDS AND EFFECT OF ACIDS ON SUGAR ON DRYING:**

*Associate referee:* L. H. McRoberts, Food and Drug Adm., San Francisco, Calif.

**PECTIC ACID AND ELECTROLYTIC TITRATION ACIDITY:**

*Associate referee:* W. H. Roberts, Office of Food Commissioner and Chemist, Bismarck, N. D.

**FRUIT ACIDS:**

*Associate referee:* B. G. Hartmann.



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### MOISTURE IN DRIED FRUIT:

*Associate referee:* Paul Clifford, Food and Drug Adm., Washington, D. C.

### VITAMINS:

*General referee:* E. M. Nelson, Bureau of Chemistry and Soils, Washington, D. C.

### CANNED FOODS:

*General referee:* V. B. Bonney, Food and Drug Adm., Washington, D. C.

### VINEGARS:

*General referee:* A. M. Henry, Food and Drug Adm., Philadelphia, Pa.

### FLAVORS AND NON-ALCOHOLIC BEVERAGES:

*General referee:* J. B. Wilson, Food and Drug Adm., Washington, D. C.

### MEATS AND MEAT PRODUCTS:

*General referee:* R. H. Kerr, Bureau of Animal Industry, Washington, D. C.

### GELATIN:

*General referee:* R. M. Mehurin, Bureau of Animal Industry, Washington, D. C.

### CACAO PRODUCTS:

*General referee:* J. W. Sale, Food and Drug Adm., Washington, D. C.

### MILK SOLIDS IN MILK CACAO PRODUCTS:

*Associate referee:* Marie L. Offutt, Food and Drug Adm., New York City.

### SHELL IN CACAO PRODUCTS:

*Associate referee:* W. O. Winkler, Food and Drug Adm., Washington, D. C.

### GUMS IN FOODS:

*General referee:* L. J. Cross, Dept. of Dairy Ind., Agr. College, Ithaca, N. Y.

### SPICES:

*General referee:* J. F. Clevenger, Food and Drug Adm., New York City.

### BAKING POWDERS AND BAKING CHEMICALS:

*General referee:* W. C. Geagley, Department of Agriculture, Lansing, Mich.

### MICROCHEMICAL METHODS:

*General referee:* E. P. Clark, Bureau of Chemistry and Soils, Washington, D. C.

### MICROBIOLOGICAL METHODS—CANNED FOODS:

*General referee:* A. C. Hunter, Food and Drug Adm., Washington, D. C.

### TREATMENT OF UNOPENED CONTAINER:

*Associate Referee:* Carl Fellers, Agricultural Experiment Station, Amherst, Mass.

### SAMPLING INOCULUM:

*Associate referee:* F. W. Tanner, University of Illinois, Urbana, Ill.

## CULTURE MEDIA OF NON-ACID PRODUCTS:

*Associate referee:* E. J. Cameron, National Canners Assn., Washington, D. C.

## CULTURE MEDIA OF ACID PRODUCTS:

*Associate referee:* B. A. Linden, Food and Drug Adm., Washington, D. C.

## INCUBATION PERIODS AND TEMPERATURES FOR CULTURES:

*Associate referee:* L. H. James, Bureau of Chemistry and Soils, Washington, D. C.

## NUTS AND NUT PRODUCTS:

*General referee:* S. C. Rowe, Food and Drug Adm., Washington, D. C.

## CEREAL FOODS:

*General referee:* J. A. LeClerc, Bureau of Chemistry and Soils, Washington, D. C.

## ASH IN FLOUR, MACARONI PRODUCTS, AND BAKED PRODUCTS; CHLORIDES IN FLOUR AND BAKED PRODUCTS; AND MOISTURE IN BAKED PRODUCTS CONTAINING FRUIT:

*Associate referee:* L. H. Bailey, Bureau of Chemistry and Soils, Washington, D. C.

## H-ION CONCENTRATION OF FLOUR:

*Associate referee:* Rowland J. Clark, 436 W. Dartmouth Road, Kansas City, Mo.

## DIASTATIC VALUE OF FLOUR:

*Associate referee:* M. J. Blish, Agricultural Experiment Station, Lincoln, Nebr.

## STARCH IN FLOUR:

*Associate referee:* V. E. Munsey, Food and Drug Adm., Washington, D. C.

## FLOUR-BLEACHING CHEMICALS:

*Associate referee:* Dorothy Scott, Food and Drug Adm., New York City.

## FOREIGN METHODS FOR TESTING FLOUR:

*Associate referee:* C. H. Bailey, University of Minnesota, Minneapolis, Minn.

CO<sub>2</sub> IN SELF-RISING FLOUR:

*Associate referee:* L. D. Whiting, Ballard and Ballard, Louisville, Ky.

## METHODS FOR MACARONI PRODUCTS, BREAD AND BAKED PRODUCTS:

## (a) UNSAPONIFIABLE MATTER:

*Associate referee:* H. A. Lepper, Food and Drug Adm., Washington, D. C.

(b) FAT, CRUDE AND ALBUMIN NITROGEN, LIPOID P<sub>2</sub>O<sub>5</sub>:

*Associate referee:* F. L. Hart, Food and Drug Adm., Washington, D. C.

(c) CRUDE FIBER IN BAKED PRODUCTS:

*Associate referee:* Ruth G. Capen, Bureau of Chemistry and Soils, Washington, D. C.

MILK SOLIDS IN MILK BREAD:

*Associate referee:* V. E. Munsey, Food and Drug Adm., Washington, D. C.

RYE IN FLOUR MIXTURES:

*Associate referee:* J. H. Bornmann, Food and Drug Adm., Chicago, Ill.

VISCOSITY OF FLOUR:

*Associate referee:* C. G. Harrel, Pillsbury Corporation, Minneapolis, Minn.

COLD WATER EXTRACT FLOUR:

*Associate referee:* F. A. Collatz, Washburn-Crosby Corporation, Minneapolis, Minn.

ERGOT IN FLOUR:

*Associate referee:* Clinton L. Brooke, Pillsbury Corporation, Minneapolis, Minn.

CATALASE AND PROTEOLYTIC ENZYMES:

*Associate referee:* A. K. Balls, Bureau of Chemistry and Soils, Washington, D. C.

COLOR IN FLOUR:

*Associate referee:* H. K. Parker, Novadel-Agene Corporation, Newark, N. J.

BEERS, WINES, AND DISTILLED LIQUORS:

*General referee:* W. V. Linder, Bureau of Industrial Alcohol, Washington, D. C.

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## WILEY MEMORIAL LECTURE. NO. III

### THE HISTORY AND VALUE OF GERMICIDES<sup>1</sup>

By A. R. L. DORME (415 Baltimore Life Building, Baltimore, Md.)

A germicide is a substance or agent which destroys germs. The word is synonymous with the term disinfectant, as both are used to indicate the destruction of microorganisms. The term germicides is also often considered synonymous with the word antiseptics. However antiseptics do not always kill organisms, and they often merely prevent the growth and activity of microorganisms; they usually delay or prevent fermentation and putrefaction. Thus, cold is an antiseptic, and will preserve meats or fruits because it keeps the bacteria in them inactive, even though it does not kill them. Disinfection is the killing of pathogenic organisms which might infect the human body. The destruction of all lower forms of animal and vegetable life whether disease-producing or not is termed sterilization. An object may be disinfected and yet not sterile, but if it is sterile it is also disinfected. Again, the same germicide that in low concentration may only inhibit the development of bacteria, in higher concentrations will kill bacteria. For example, mercuric chloride in 1:100000 solution will inhibit the growth of anthrax, while a 1:1000 solution will kill it.

Sunlight and dryness are nature's germicides, and few if any pathogenic germs can survive direct sunlight or perfectly dry air.

Germicides are limited in number and rather specific in effect, because those that readily kill bacteria destroy human body cells still more readily and hence cannot be used internally or, in many cases, even externally. Thus, our oldest and standard germicides are phenol and mercuric chloride, but they are deadly poisons to tissues and human life when used internally, and except in high dilution are damaging to tissues, skin and mucous membrane when used externally.

Until quite recently there was really no means available to combat and destroy the deadly germs that make a fine meal of some part of a patient's body. What was done prior to and in the early days of the nineteenth century was to treat the symptoms of such a disease, ameliorate the pain and the fever and the distress of the patient, and trust and hope that the so-called *vis medicatrix naturae*, the vitality of the patient, would win the battle. Even if the doctor did locate and diagnose the disease correctly, the best he could do for measles, typhoid, scarlet fever, pneumonia, whooping cough, rheumatism, influenza, erysipelas, etc. was to look wise and prescribe some drugs to relieve pain, reduce fever, induce perspiration, move the bowels, etc., which is merely treating symptoms.

<sup>1</sup> Presented at the Annual Meeting of the Association of Official Agricultural Chemists, held at Washington, D. C., November, 1933.

In practically all these diseases and in dozens of others the cause was not known, and if it were known, the means to combat it successfully, that is destroy or remove it, was not known. Therefore, in those days the doctor who could successfully encourage the patient to fight the disease by making him think he was better and would get well, that is to be a psychologist and an optimist as well, was the best doctor for any patient. To be sure to have a great diagnostician like Osler, who could determine the cause of the patient's condition from long experience, keen observation, a discerning mind, and a great fund of knowledge, was a decided advantage. To know what you are fighting makes what you can do and should do much more rational and effective, even though you realize that the best you can do will only ease the discomfort and improve the chances of a patient in fighting the bacteria that are multiplying and making a major attack on his vital organs.

#### LOUIS PASTEUR

Such was the condition of affairs in 1857 when the great research genius of medicine, Louis Pasteur, came on the scene in Paris. He had not shown any great brilliance in his college work and even in chemistry was only marked mediocre in his Bachelor of Science examination at Dijon at 20 years of age. It was not until he attended, at the Sorbonne, the lectures of the great chemist Dumas, lectures which drew 700 people at times, that Pasteur became inspired to begin research work and changed from a quiet philosophically minded student to an enthusiastic chemist delving into the unknown. His first work was on the dimorphism, as he called it, of tartaric acid, in which, by closely observing the small unsymmetrical hemihedral crystal faces that determined the laevo or dextro rotatory power of the substance and of their mixture, paratartaric acid, with no rotatory power, he solved the cause of this variation in rotatory power.

Medical men had known before Pasteur's time that fevers spread and increased among the people as did epidemics and that a disease could be transmitted through clothing—in short that there was something alive, a *contagium vivum*—that spread disease. This view was not new, as it had been stated in the sixteenth century by a Veronese physician, Frascatorius, who spoke of the seeds of contagion passing from one person to another and compared contagion and wine fermentation. This was fully a hundred years before Leeuwenhoek first saw animalculae or infinitely little things in water through his home-made microscope.

#### FERMENTATION

The crystallography of tartaric acid led Pasteur while at Lille to study wine fermentation, in which this acid is produced. Out of this work came his papers on lactic acid fermentation and alcoholic fermentation, in which he proved that this action is the life process of a ferment-yeast. It feeds

on sugar and exhales carbon dioxide and alcohol. After winning the long fight against spontaneous generation as the cause of these changes by invisible agents, he pondered over the question as to whether disease may not be like wine and be carried by an invisible agency, or as he said "minute living organisms." Said Pasteur: "Is not putrefaction in the body"—by which he meant degenerative changes followed by pus formation—"identical with fermentation?" It was when Pasteur proved this theory that Lister made of surgery an exact science by learning to avoid the infections in operative work. Pasteur next discerned the infectious nature of the silkworm disease and worked out the secret of the fermentation of vinegar and of the diseases or errors in beer fermentation. Next he filtered air through cotton and found that such air did not produce growths of bacteria in bouillon, while air of Paris not so filtered did produce bacterial growths, and that these growths changed the bouillon. As the bacteria had fed on the bouillon and changed it, so in the body bacteria probably fed on its tissues and changed these. Might not, reasoned Pasteur, their excretions be poisonous to the human body and the product of their life process generate poisons that would cause the death of the patient.

At this time, 1876, Robert Koch proved that anthrax was caused by bacteria, and for the first time isolated the bacterium of anthrax in pure culture, proved its spore formation, produced the disease in animals by inoculating them with this pure culture, and finally extracted the anthrax bacteria from the diseased animals. This finding, which made Koch famous, proves the connection between bacteria and disease. It is now called the Koch cycle.

Pasteur repeated and confirmed Koch's results, and it was at this period of his notable experiences that he made what was probably his greatest discovery—that if an animal could be inoculated with the attenuated poison or virus produced by anthrax, it would get only a mild attack of the disease and survive. The virus was weakened by feeding the bacteria improper or inferior food. Pasteur had applied to anthrax the principle established by Jenner in 1796 for smallpox and proved that inoculating or vaccinating an animal with attenuated virus would protect it from death from this disease. In 1881 Pasteur tried this anthrax inoculation on sheep with the result that those that were inoculated survived while those that were not inoculated died. This so impressed the scientific world that at the International Medical Congress of 1881 Pasteur shared the highest honor and applause with Rudolf Virchow, whose monumental work in cellular pathology had revolutionized the physician's conception of the nature and course of disease. Finally, the work on rabies topped the great career of Pasteur, created the Pasteur Institute in 1888, saved hundreds of thousands of lives, and caused him in 1923 to be acclaimed by the vote of every registered voter in France the greatest Frenchman that had ever lived.

Pasteur had shown (1) that every fermentation is caused by the growth and life process of a special microbe which has become mixed with the article fermented; (2) that every infectious disease is probably caused by the development within the organism or body of a special microbe; and (3) that this microbe of an infectious disease may by culture be attenuated or weakened under conditions undesirable to its growth, and its pathogenic activity thereby so weakened that from being a virus it becomes a vaccine, that is a remedy to prevent the disease becoming virulent in those infected by it.

### SERUM TREATMENT

The cause of disease had thus been established, but as yet little or nothing was known about germicides. Next came the discovery, in 1884, of the diphtheria germ, the Klebs Loeffler bacillus, and the serum method of treatment of diphtheria. This serum treatment consists of the injection into the patient of the serum of a horse that has had injected into its system great quantities of the toxin or poisonous secretion of the bacillus of diphtheria and meets this invasion by developing in its blood an antitoxin that neutralizes the toxin and prevents it from poisoning the horse. This antitoxin serum is injected subcutaneously into the blood of a patient suffering from diphtheria, where it neutralizes the toxins liberated into the blood by the life process of the bacillus. These toxins usually kill by poisoning the heart. At the present time this serum treatment is used in several diseases, such as diphtheria, typhoid, scarlet fever, anthrax and tetanus. However it does not destroy the germ, that is, it is no germicide; it only neutralizes the poison or toxin the bacillus secretes. In some cases the toxins are not secreted by the germ but are contained in the germ, as in typhoid, cholera, or tuberculosis.

The germicides known in the early days were quinine for the malaria plasmodium, mercury for the spirochete of syphilis, iodine, and iodoform. Iodoform was almost universally used by surgeons, who could almost always be recognized by its powerful odor. It is now known to be ineffective as a germicide. In those days, however, quinine and mercury were not known as germicides, but as remedies. Iodine, although used as far back as 1820, by Coindet, was found too strong when used undiluted, and later was superseded by tincture of iodine, in which form it is now considered to be an effective germicide for external use only. It has certain advantages due to its power of spreading its effect over an area. Iodine has also been used as a germicide to some extent in the form of Lugol's solution, which is an official 5 per cent potassium iodide solution of iodine in water.

In 1881 Robert Koch discovered that mercuric chloride had the power to kill germs, and it was gradually introduced into surgery and medicine as an effective germicide, although because of its very poisonous nature it could only be used locally and externally.

Then phenol made its appearance as a germicide, and it has since been generally used for this purpose, although it is also limited to external use and in strength to be effective, because of its toxicity.

Alcohol was also found at this time to be a germicide, but because of its toxicity when used internally, it has been employed only for external use, for which purpose, however, it is very effective.

#### METALS

Some of the metals were next found to be germicidal in form of silver foil or colloidal gold or silver, but again available only for external use. Then came silver nitrate as lunar caustic or in 10 per cent aqueous solution, effective to be sure but very caustic and suitable only for external use. Following these products came the various organic silver compounds, such as argyrol, albargin, silvol, etc., which have found considerable use in certain nose, throat, eye, and ear infections. The creosol group of products, derived originally from creosote, have also found adoption largely, however, as disinfectants rather than as germicides. Creosol carbonate, guaiacol carbonate, and pure creosol and guaiacol were for quite a period used as specific agents for pulmonary tuberculosis, the theory being that taken internally they would be liberated as such in the lungs and destroy the tubercle bacilli there. What favored this theory was the fact that when so taken, the breath of the patient would smell of guaiacol and creosol. The desired curative effect on the patient's tuberculosis was not observed, however, and so these remedies gradually faded from the picture.

Soaps, especially tincture of green soap, possess germicidal powers to a limited degree and have been used mainly as detergents. So-called germicidal soaps, with weaker germicides such as resorcinol, or stronger germicides such as mercuric potassium iodide, are used with some success in sterilizing the hands of the surgeon or in alleviating certain skin troubles.

By this time bacteriology had advanced sufficiently to bring the aniline dyes into the field as staining agents of the microorganisms being studied under the microscope. Then it was observed that some of these dyes killed bacteria; and gentian violet, malachite green, brilliant green, fuchsin, and others became known as germicides. They are, however, not true germicides; rather are they antiseptics, that is they act bacteriostatically by inhibiting the action of the germ. They are not used for internal medication but for application on mucous membranes, as well as in the treatment of suppurative skin diseases and of burns.

#### ARSENICALS

We now arrive at the arsenical period in the beginning of this century, when atoxyl, or sodium para-aminophenyl-arsonate, was introduced for

sleeping sickness, trypanosomiasis and syphilis, with the reservation again of the danger of arsenic poisoning, as it can only be used subcutaneously.

Then came the great Ehrlich, who, after synthesizing 605 new substances in an effort to produce an anti-syphilitic, finally for his 606th effort produced salvarsan or arsphenamine, or as it was first named, 606 (dioxydiaminoarsenobenzol dihydrochloride), an arsenical organic product, as was atoxyl, which has the power to kill the spirochete of syphilis. Here again the danger of arsenic poisoning makes its use a great care for the physician, because skill is required in its administration, which is intravenous, to avoid poisoning the patient. It contains about 30 per cent of arsenic. Neoarsphenamine is a mixture of several salts including sodium-diaminodihydroxyarsenobenzol methanal sulfoxylate; it contains about 19 per cent of arsenic, but being weaker than arsphenamine it is less dangerous.

The World War produced the hypochlorite group of germicides headed by Dakin's solution and dichloramine-T and later followed by Zonite, but these products are so likely to oxidize to chlorites that they lose their efficacy on standing for any length of time. When freshly prepared they are effective germicides, but they, too, are available for external use only.

Boric acid, borax, hydrogen peroxide and potassium permanganate have been used at times, the former especially for eye conditions, but none of them has any real germicidal value, although potassium permanganate is useful as an insecticide for plant bulbs and plants.

Resorcin or resorcinol has some use as a germicide in skin conditions, but its germicidal power is so low (a phenol coefficient of 0.3) that it is but little used by physicians.

#### MERCURIALS

We now come to the group of the mercurial germicides that have dye-stuffs or other organic compounds containing mercury in their molecule. It is necessary to use all of them with care because of the mercury, and hence they are more especially adapted for external use. The first one was phenyl mercuric nitrate ( $C_6H_5Hg NO_3$ ), containing 60 per cent of mercury. It was first produced in 1870, but it was not developed as a germicide until very recently. Its germicidal power is very great both for external and internal use, and it is not materially reduced by organic matter nor does it affect the substances it is intended to preserve. The risk is largely due to the toxicity of the mercury when taken internally, but it has been successfully used intravenously in animals.

Then came Mercurochrome (disodiumdibrom-oxymercuri-fluorescein), a dyestuff to which is added an atom of mercury, produced by Davis and White approximately 15 years ago and used largely for external use for infected surfaces, but to be used with great care internally or by injection. It contains 24 per cent of mercury.

Metaphen (diacetoxy-mercuri-4 nitro-2 creosol) contains about 60 per cent of mercury, is insoluble in water and for solution alkalies are used. This strong germicide is used successfully in gonorrhea and eye infections, for sterilizing instruments, and for external use.

Methiolate, or sodium-ethyl-mercuri-thiosalicylate, is a germicide that possesses value under certain conditions. It contains about 50 per cent of mercury and must be used with care, especially if used internally.

Mercuraphen, or sodium-oxy-mercury-ortho-nitro-phenolate, contains about 50 per cent of mercury; its decided germicidal strength can be utilized for gonorrheal infections, for sterilizing instruments, and for all surface infections, but as in the case of the other mercurial germicides it should be used with care in internal treatment.

Methenamine or hexamethylene-tetramine has for many years been used as a urinary antiseptic because it liberates formaldehyde in acid urine and then only in large doses. If the urine is not acid it is not effective.

Acridine, or 3, 6-diamino, 10-methylacridinium chloride-hydrochloride  $C_{14}H_{14}N_3Cl \cdot HCl$  and  $H_2O$ , is a dye made from acridine. It is a strong germicide used externally for wounds, as a gonorrheal injection, and for other irrigation purposes.

Pyridium, or phenyl azo- $\alpha$ -diamino-pyridine hydrochloride, is a germicide used mainly for external applications to wounds and internally as a urinary antiseptic, when it is excreted unchanged. It is also sold under the name Malaphen.

#### ALKYLRESORCINOLS

The status of germicidal history in 1923 was that few if any germicides were known that exceeded the strength of 20 in phenol coefficient, which is a standard and method of comparing the germicidal strength of products now in general use, based on comparison with phenol. The germicide must be soluble in water to be available for this test, and the relative amount of the tested germicide in water is compared with a definite amount of phenol in solution, both being applied to the bacillus typhosus of standard culture supplied by the government's Bureau of Chemistry. A ratio or coefficient is obtained by testing various dilutions of the germicide until one dilution ceases to prevent bacterial growth on a petri dish culture medium of standard formula. The result is a number, say 40, representing this phenol coefficient or ratio, and such number becomes the phenol coefficient of the germicide.

Germicides continue to be graded and classified according to their value by their phenol coefficient (Rideal-Walker test), but considerable objection has been raised against this method because by it only phenolic substances can be satisfactorily determined. Arsenicals and mercurials do not lend themselves to this technic or to any of its modifications. Another objection probably justly raised against this method is the fact that



it employs only one germ, the bacillus typhosus. It is well known that many germicides show varying effectiveness to different germs. Therefore a more satisfactory test would include a variety of germs, say B-typhosus, B-staphylococcus aureus, B-streptococcus viridans and B-coli, and finally the average coefficient of the results obtained for each of these germs.

It was in 1923, through the suggestion of Dr. Veader Leonard of Baltimore, that my attention was directed to a substance which he had in impure condition and desired me to purify so that he could work on it in the bacteriological laboratory of the School of Hygiene at Johns Hopkins University. Out of a study of this substance, propyl resorcinol, with a phenol coefficient of only five, developed the synthesis in my laboratory of the whole series of normal alkylresorcinols and many isoalkylresorcinols. The work of Dr. Leonard and also that of his associates demonstrated that these alkylresorcinols possess high germicidal power, which increases in a regular curve as the alkyl molecule grows larger. Thus propyl is 5, butyl 22, amyl 33, hexyl 72, heptyl 300 in phenol coefficient, and thereafter the insolubility in water prevents testing. To make the problem more important as well as interesting, the toxicity of these alkylresorcinols decreases as the molecule of the alkyl increases in size. Thus the methyl and ethyl are toxic, but the propyl only very mildly so, and the butyl, amyl, hexyl, etc. are non-toxic. As usual, the solubility of these products in water decreases with the increasing size of the alkyl chain. Of all these alkylresorcinols, the hexylresorcinol, with a phenol coefficient as high as 72, proved the most effective, which means that the white crystalline substance is 72 times stronger than phenol in germicidal power. At the same time the substance is non-toxic and has no deleterious result on tissues or vital organs of the human body. Here for the first time were produced germicides of great power that can be freely used both externally and internally, and that are perfectly safe in the hands of any one. It has been shown that these alkylresorcinols destroy practically all known germs and spores on mere contact, and the problem of the clinician is to so prepare them that they will reach the seat of infection and the germs in any lesion in the body. It is for this reason that for perhaps the first time the American Medical Association, after checking up the remarkable results obtained and published in medical journals, advised and endorsed the general public use of this germicide, hexylresorcinol. The unusual properties of this product, as well as of many other medicinal and food products have been questioned recently in a sensationally written publication. As a rule the condemnation is in general terms, but in the case of germicides it is based on one published paper, which is practically universally regarded as unreliable because the technic described is faulty. So as far as hexylresorcinol and all the products into which it enters as a germicide and antiseptic are concerned, all the printed and published

statements have been carefully checked by disinterested scientific experts and in every case have been confirmed.

These alkylresorcinols proved to be the ideal germicides, as defined by Rosenau, and to be the ideal urinary antiseptics, as defined by Davis. Thus, Rosenau says that the ideal disinfectant must have high germicidal power, must be soluble in water, should be harmless to man and animals, should have the power of penetration, and should not corrode metals, bleach pigments or stain surfaces. This description applies rather to disinfectants than to germicides. Davis, however, refers to germicides in his definition of a perfect urinary antiseptic as follows: "1—It should be chemically stable. 2—It should be nontoxic. 3—It should be non-irritating to the urinary tract. 4—It should exert an antiseptic action in high dilution in urine of any action. 5—It should be eliminated in high percentage by the kidney."

Hexylresorcinol was also found by Lamson and his fellow-workers at Vanderbilt University to be a specific for hookworm and intestinal worms after they had worked with partial success during twenty years on thymol, carbon tetrachloride and many other substances. Thus, gradually, through experimentation and research, a way will be found to get this product, which destroys all germs and their spores on mere contact with them, in a form that can be used effectively for the germs of other diseases. It also required Lamson's work to prove that it can be taken in 20 grain doses repeated, as before this time it was not thought possible to use it in crystal form or in large doses.

#### FUTURE WORK

We thus find that the value of germicides in the urinary tract and the intestinal tract and for wounds or mucous surfaces has been established. No germicide for the blood that is safe and has the approval of the medical profession is yet available. If we had one that when injected into the blood stream would destroy germs, we could save many lives that now pass out by blood poisoning. But this accomplishment will come as soon as efforts succeed in getting the germicides we have in form to reach the part of the body where the lesion, or point of attack of the germ, is located; as for instance, the lung in pulmonary tuberculosis. Such a technic might involve attaching the germicide chemically to a dye that we know has a specific affinity for and stains the tubercle and its tissues in the lung, so that the dye would take the germicide to the lung. Perhaps, the dye would then decompose and liberate the germicide, or the dye-germicide compound might be in itself a germicide to destroy the tubercle germs in situ. We thus see the great possibilities of enlarging the uses and effectiveness of such germicides as are in themselves not toxic or destructive to body tissues. There are practically no limitations, by synthesis or research on substances already known, to the making of products that will aid the physician in his fight against disease.

Surgery was revolutionized by Pasteur's work and Lister's application of its results, and the World War also materially advanced the possibilities of surgery owing to the mass of material at hand and the risks taken when the patient was doomed any way. In the same way medicine, or the attack on disease by medicinal agents, is almost sure to make decided progress and the number of specifics for diseases continually to increase, with the result so devoutly to be wished, that medical men will have a real agent to attack successfully most of the diseases flesh is heir to.

In this advance and progress germicides will play an increasingly important part because most of our scourges and dangerous diseases are either now known to be due to some microorganisms invading the human body or will be found to be due to such cause. There are at least three methods of defeating the attack of these germs upon the human body: (1) neutralizing the poisoning produced by the toxins secreted by the germs by injecting antitoxins into the body; (2) vaccinating the patient and producing a mild form of the disease by such vaccination, thus producing anti-bodies in the patient; (3) destroying the germ causing the disease by giving, applying or injecting a germicide harmless to tissues and organs. The last method would be the most effective, the least dangerous, the most rapid and the most rational mode of attack, and its successful realization awaits the discovery of a strong germicide that is harmless to tissues and organs and can be used effectively in tissue and blood stream without detrimental result or danger to life. That such a substance exists or can be produced by synthesis is undoubtedly true; the problem is to find it and demonstrate definitely its ability to destroy all pathogenic germs without injury to, or loss of germicidal power in, the blood stream or tissues of the human body.

## PRESIDENT'S ADDRESS<sup>1</sup>

### THE REGULATORY CHEMIST OF THE PRESENT AND FUTURE

By JAMES W. KELLOGG, (Director-Chief Chemist, Bureau of Foods and Chemistry, Harrisburg, Pa.)

The Association of Official Agricultural Chemists of North America was established primarily to afford an opportunity for official chemists to gather in annual conference to discuss their mutual problems, to report the results of their researches and investigations, and to adopt accurate and reliable methods of analysis, and for 49 years these chemists, honored with membership in this unique and important Association, have assembled in conference to fulfill their rights and privileges.

It is indeed an honor to be a chemist employed by any national, state or provincial institution or body charged with the enforcement of control laws regulating the sale of foods, dairy products, drugs, medicinal preparations, caustic poisons, paints and painting materials, fertilizers, feeding-stuffs, insecticides and fungicides and other products relating to agriculture.

We are a unique association because eligibility to membership is contingent upon being a chemist, bacteriologist, microanalyst or other scientist employed by these institutions. An untrained regulatory official or enforcement appointee is not eligible. By virtue of the official position no dues are assessed and membership continues until the official position terminates, or the chemist has returned to that inevitable state of dissolution, where matter fails to show any evidence of detectable motion or activity, according to accepted official methods of analysis.

The work accomplished by this Association, largely the adoption of official methods of analysis for the products coming within the scope of our control laws, has been of the greatest economic importance, and it has received world-wide recognition from all agricultural chemists as well as from Courts where legal controversies are involved. During its 49 years of service many control problems have been solved. The problems of the present are varied, and they continue to increase, in number and complexity; therefore, if we can form any judgment or opinion from past and present experiences, the work of the future is destined to increase in like proportion. From a few official methods adopted to apply to fertilizers and dairy products, our field has enlarged to such an extent that we now have a book of official methods of 600 pages, including 744 official methods of procedure for about 40 different types of materials or products.

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<sup>1</sup> Presented Tuesday afternoon, November 7th, as special order of business for 2 o'clock.

Inasmuch as we are engaged in studying methods of analysis, it is only proper that we should extend our researches to ourselves and attempt an assay of what a regulatory official chemist really is, what his qualifications and duties are, and what must be accomplished, to the end that we may properly fit into the picture of the "New Deal," successfully meet the new problems which the future has in store for us, and thereby be worthy of the service and accomplish the results so necessary for effective and efficient law enforcement work.

The officials, chemists, and other scientists engaged in law enforcement work may be classified into three groups or lines of specialization as to duties performed, namely, the regulatory official, the regulatory chemist and the research chemist.

There is a marked difference between these classes of officials, especially with respect to their qualifications and duties. The plain ordinary garden variety of regulatory official is usually not a chemist, in the recognized meaning of the term; rather he is an official charged with the administrative or executive phases of enforcing food, dairy and agricultural control laws, depending upon the chemist for sufficient knowledge to carry on. He may be a splendid executive, and besides being a capable and efficient enforcement officer may have appreciative understanding, broad vision, and ability to interpret reports or methods of procedure, usually technical in character, requisite for efficient service. On the other hand, he may be a person lacking in these qualifications (and there have been such cases) and not even have the necessary training, experience and personality to enable him to supervise control work.

The regulatory chemist, or the official chemist, bacteriologist or microanalyst, is one who has been properly trained along scientific lines in recognized schools and colleges according to well-defined standards, and either has been placed in charge of law enforcement work, or is associated with it, in those institutions where official work is performed. In any event, he is at least a trained scientist, and because of his training and official position is entitled to membership in this Association.

The research chemist, engaged in, or associated with, official enforcement work, should not, as a rule, be required to be a law enforcement officer. His duties should be those incident to solving special problems or working out details of the methods of analysis upon which are based the standards, definitions and uniform procedure required in successful law enforcement work.

Research requires special equipment and the devotion of trained chemists for long hours of labor, whereas regulatory work is largely administrative in character and is dependent for success upon the intelligent application of the results of research work in special fields to the economic features involved, in preventing misbranding and the sale of inferior quality products.

It is important, therefore, to understand definitely that there should be a clear distinction between the duties and qualifications of the official chemist charged with the administration of regulatory work and those of the research chemist. The research chemist, of course, may also be the enforcement officer, but his duties should primarily be analytical and investigational in character. It is the official chemist, therefore, whom we shall examine by such tentative methods as are available, in an effort to decide his present status and requirements and his adaptability to solve the problems at hand, in order that we may determine what training, requirements or qualifications shall be considered requisite to qualify an official chemist to meet the problems of the present and future.

The official chemist must be thoroughly trained in recognized institutions and have a reasonable amount of experience and understanding in order that he may comprehend the essential phases of research work and the requirements of control laws and have the ability to apply this information to these activities in an effective, practical and economical manner. The official chemist must be versatile. Integrity, personality, and adaptability are necessary attributes in gaining the confidence of the public, and at the same time comprehending the problems of the manufacturer. He should understand the technicalities of processing many products and become familiar with some of them, for example, bakeries and ice cream and bottling plants, with respect to sanitary methods of procedure. He should be able to assist in the preparation of standards, definitions and the various codes required for the uniform regulation of industry. By virtue of his position, he will be called upon to take an active part in the formulation of laws, regulations and methods of procedure, so that in enforcing the laws and regulations he may be able to carry out the intent of the laws as well as the desires of the public in a practical manner and thereby prevent fraud and deception. Because of the multiplicity of these duties, the official chemist can not hope to engage in research work, even though he may be scientifically trained. He must depend on research chemists for the information required, and if it is possible, he should establish separate agencies to carry on the details of research work.

Therefore, in order to function properly, that is obtain the information required to make control laws practically effective, we must have research work performed by specially trained scientists and then apply the results of this research to the adoption of practical methods of analysis. These methods may then be employed in the examination of products coming under our supervision, in order to determine their essential characteristics or physical or chemical properties, and this information, in turn, be properly coordinated with trade practices.

It is the duty of the regulatory official to cooperate with the manufacturers that are putting out quality products, and complying with the law, in order to prevent other manufacturers that are not putting out

products meeting the standards and requirements from engaging in unfair competition.

Regulatory work is of the greatest importance because it enters directly into the economy of industry within the scope of the products covered by control laws, and also because it directly affects the public health and the pocketbook of all consumers. One of the outstanding examples of this economic and health protecting work has been the saving of millions of dollars and the prevention of disease and death to many people by the adequate control of the milk supply. The prevention of poisoning from arsenic and lead-sprayed fruit and the protection of the fruit industry itself have been the direct result of this particular phase of control work. If it were not for the research work accomplished, and the effective control methods used in preventing ripe olive poisoning, great losses to the growers and untold illness and death to the consumers would have resulted.

Regulatory food and drug work, while similar to ordinary municipal police control, must be considered of far greater significance to the economic structure. The police departments throughout this and other countries, organized to prevent crime, are distinctive enforcement officers, yet they depend to a large extent upon the results of the research conducted by their special detective service to solve crime. Effective control, therefore, is founded on carefully conducted research and investigation. It follows that unless methods of analysis, standards, and definitions are as nearly perfect as is possible, the economic factors and proper safeguarding of the public health will be vitally affected. We can not operate a car at a high speed on an irregular or poorly constructed highway, and by the same token we can not hope to drive a true course, or guide industry into correct labeling habits, without smooth and uniform methods. We must have uniform dependable standards and definitions as guides, a track on which to travel which is clear and sound in every respect. Moreover, the methods which we shall adopt in the future must, as in the past, be recognized by all official chemists and the courts. These methods are, in fact, principles and practices of agricultural chemical procedure and represent the result of the fine devotion of chemists and other scientists to their official duties and their interest in this Association.

If we are to make progress in the future and be properly trained and competent to solve these problems, we must diligently continue this research and investigational work and apply this knowledge in a practical manner. There will undoubtedly be a marked increase in the number of official methods and in the size of our book of methods if we find methods of analysis that can be depended upon.

The 300 or more food and drug standards and definitions adopted by the National Food Standards Committee, which have also been adopted by most States, have been of the greatest value in correcting misbranding and the sale of inferior products.

We learned many years ago in our studies of the principles of economics that bad money drove good money out of the market, and at that time we could not thoroughly understand this principle, perhaps because we had very little money either good or bad. We now, however, understand this principle, and the lesson is the same in industry today. If misbranded or inferior products are permitted to be sold in unfair competition with quality products, truthfully labeled and of accepted standards, no manufacturer of such quality products attempting to meet this unfair competition can long remain in business. This is what the President meant when he stated that if 10 per cent of an industry failed to comply with the laws and principles of the various codes that have been or are to be adopted, the other 90 per cent could not meet such unfair kinds of competition and remain in business.

This is one of the problems of the regulatory official. He should cooperate in every way with industry, help to maintain the quality producer in business, and teach the "chiseler" (which word is now in good society) the error of his ways or make it impossible for him to continue in business.

The economic or official character of this work is becoming of greater importance each day. This may be illustrated by the regulations in effect in many States requiring supervision over the operation of the Babcock tests in milk plants, because upon these tests depends the correct payment to producers for the milk delivered, involving millions of dollars each year. The control chemist is required through his deputies to be thoroughly familiar with the practices in these plants, and any oversight or neglect in sampling, correct testing or following of uniform methods of analysis will result in great losses to the producers as well as to the plants themselves.

Looking to the future and having in mind that new legislation will bring more and more regulations for the control and sale of certain commodities, as, for example, cosmetics, included in the proposed new National Food and Drugs Act, together with provisions for controlling false statements and claims made by means of advertising and the radio, we realize that our problems will increase. We shall be called upon for more extensive research upon which to base uniform and official chemical, microchemical and similar methods of analysis, which, in turn, are absolutely necessary in providing for standards and definitions. We shall be required to become familiar with the varying processes of manufacture of more products than we have ever been in the past, but there are many questions which we must solve in the immediate future if we prevent misbranding, unfair competition and economic losses. A few examples of these problems will be of interest.

What does the word "fresh" mean as applied to orange juice, meat, fish and eggs? Will one company be permitted to call orange juice, pressed from the fruit six or eight months ago "fresh," and compete with another



company bottling an orange drink, the juice for which has been pressed from the fruit within 24 hours of bottling? By what methods can be detected the difference between these two types of beverages? How are we going to tell whether an egg is in fact "fresh" if no detectable deterioration has occurred, and in the case of a rather ancient egg, under what conditions its age has been acquired?

We know how to assay with some degree of accuracy milk labeled to contain 160 Steenbock units of vitamin D added to the milk in the form of a concentrated vitamin-carrying product. When, however, a milk plant irradiates the milk, claiming nothing is added, and puts such a milk on the market labeled to contain vitamin D or sells a milk produced from cows fed on yeast, similarly labeled, by what means shall we measure the potency for effective control? Or by what official methods shall we determine the potency of milk produced from cows fed a ration containing iodine, and labeled "Iodine Milk?"

In an effort to prevent the sale of processed dill pickles for genuine dills, by what quick methods can we answer this question?

When eggs that have been rejected from incubators after 18 days of incubation are used in the baking industry in lieu of fresh eggs, and claims are made that such bakery products are prepared from quality products, by what means or methods of analysis shall we determine the presence of this objectionable type of eggs?

What methods of analysis shall be employed for determining whether or not the filling of sausage is cracklings derived from the ordinary packing-house industry, or whale cracklings resulting from the rendering of whale oil?

How shall we determine whether or not the meat in sausage sold for pork sausage is pork, and what workable method will bring to light the presence and amount of skimmed milk powder used as a filler in sausage?

The definition for "custard ice cream" calls for a definite proportion of egg yolks, and by what methods shall we determine the amount actually present?

What is a pure apple jelly and how shall we prove that the jelly used in a jelly-roll, or jelly-doughnuts, sold as a pure jelly product, is in fact a synthetic product made up of pectin derived from apple pumice as a base, with added fruit acids, artificial colors and other products?

How can we tell whether or not so-called "vanilla ice cream" sold as such and flavored with a few drops of imitation vanilla flavor, is misbranded?

What shall the standard be for "butter cream" bread, "malted milk" bread, and "potato" bread, and by what official methods of analysis shall we determine whether or not the correct proportion of butter, cream, malted milk and potatoes is employed in the preparation of these types of bread?

These and many other similar problems need to be solved in the very near future. The methods of procedure adopted will depend upon careful research work, and the application of accurate methods to products under examination will help to improve quality and prevent misbranding and adulteration. Many of our methods of analysis are not adaptable for quick work, so necessary for effective control, and in the search for new methods this fact should be kept in mind.

The future of the control official, therefore, is fraught with great possibilities for service, and the members of this Association will be required to prepare themselves to meet these new problems and intelligently strive for the best interests of all concerned. Out of his experience must come improvement in methods of branding, as well as the correction of inaccuracies in present control laws.

The present National Food and Drugs Act, passed in 1906, has been a mighty force in protecting the public health and preventing misbranding and adulteration of foods and drugs entering into inter- and intra-state commerce, but the officials as well as the trade are now convinced that this Act should be amended, if certain present evils are to be corrected. If this measure becomes a law and if proposed legislation controlling the sale of a wide field of commodities becomes effective, then the work of the control officials will be increased in proportion.

Another feature of our activities of great importance, in fact one of the outstanding difficulties of law enforcement work, is the lack of sufficient funds to come anywhere near making effective the provisions of these several laws. Officials now have about all the responsibilities and duties which can be assigned to them, and they can not possibly hope to perform these duties with the means at hand. This situation explains one of the reasons why an official can be criticised for failure to fully enforce the laws, or to prevent the sale in his community of misbranded products. He knows well enough why this is so, but the public does not know it. Frequently, however, by means of certain types of publications the public is made acquainted with the official's supposed shortcomings. Therefore we may be called upon in the future to explain these misrepresentations and to bring to the attention of those responsible the need for adequate support, in an effort to overcome such unwarranted criticism.

Our present methods of procedure in the several States, as well as within the Federal departments, will probably not permit private interests to support official law enforcement work, because of the possibilities of misunderstanding and biased judgment. However, it seems reasonable for a company that manufactures a quality product to spend a definite amount of money for protecting his product by supporting law enforcement work, as has been done in some cases. It is much better for a manufacturer to spend part of his profits in such activities than to lose these profits. However, it ought not to be the function of the manufacturer to

perform the service of policing the State to prevent unfair practices. Official regulatory work should be brought about by the education of the public, to the end that this service may be adequately supported by those agencies of government created to protect the interests of all the people all of the time.

In referring to the need for funds for this type of work, the question of carrying on the affairs of this Association, as well as protecting the interests of industry, may be considered. As previously cited, no personal dues are assessed, the funds for carrying on the activities being mostly dependent upon the sale of *The Journal* and *Methods of Analysis*. It would be splendid if some provision could be made for an endowment fund, and the income therefrom used to pay for the services of the secretary and editors and to assist in financing the research and other work of this Association.

There is not an organization or association in the country today which is of such vital economic importance to the public at large and to the industries involved as this Association. The correctness of methods of analysis and the intelligent enforcement of control laws are of the greatest economic value for according to them, industry and consumers may either be fully protected or may lose vast sums of money and be cheated in the value of the goods produced and consumed. If it is not possible for the Nation or the States, by reason of legal entanglements, to provide for the affairs of this Association, then it certainly would not be improper, unethical or out of harmony with its traditions, for private agencies to aid in furthering its work. In order that this valuable service, as planned by those who have devoted their lives to pure food work, may be advanced, it is hoped that those interested may find it possible in the near future to provide an endowment fund.

I am convinced that there is a great future in store for the official chemist, bacteriologist, microanalyst and other scientists engaged in this official work, and that there is an opportunity for a continuance of this splendid service. We need patience, courage, training, versatility, resourcefulness, personality and many other qualifications. It is a big order for a big job, but keeping in mind these essential qualifications the regulatory official in the future will, I am sure, not only bring about a "New Deal" in law enforcement work, but will carry forward with increased service and great honor the name of this Association.

## ORDER OF PUBLICATION

The reports of the committees presented on the last day of the annual meeting are given at the beginning of the proceedings, not in their chronological order. This arrangement will assist the referees, associate referees and collaborators in planning and developing their year's work. The remainder of the proceedings will then follow in the usual order.

### THIRD DAY

#### WEDNESDAY—AFTERNOON SESSION

##### REPORT OF EDITORIAL BOARD

The index of the proceedings of the Association since its organization in 1884 and including the three editions of *Methods of Analysis* and *The Journals* will be sent to the printer after it has been typed. The entries are completed, but a little further checking back is necessary. In addition to the sum of \$465 expended last year for this work, \$180 was spent this year. An original appropriation of \$1000 was made by the Executive Committee, and it is expected that this amount will cover the cost of printing also.

Dr. Blanck will report for the Editorial Committee of *The Journal* in the absence of W. S. Frisbie, *Chairman*; Dr. Le Clerc will report for the Committee on *Methods of Analysis*, and Dr. Browne for the Committee on *Principles and Practice of Agricultural Analysis*.

W. W. SKINNER

##### REPORT OF EDITORIAL COMMITTEE OF THE JOURNAL

At the meeting of the Editorial Committee of *The Journal* held recently the matter of cutting down the copy on reports as much as possible and allowing more space to the Contributed Papers section was discussed, and it was decided that this should be done whenever possible.

The subscription list shows a greater reduction this year than has ever occurred. The loss of domestic subscriptions was 65 and of foreign 36, the places sending the most cancellations being New York, 14, and Russia, 19. New subscriptions were 9 domestic and 5 foreign. Last year Volume XV contained over 700 pages and the cost of publication was \$3,966.13; this year the pagination is approximately 650 and the cost of publication approximately \$3,438.99.

We are only \$165.52 short of the publication cost this year, and our Board of Editors thinks this quite a satisfactory showing. On the advice of the printer we took advantage of current prices to buy paper for next year's journals, thereby saving a substantial sum. The Editorial Board also decided to have the subscription rate for subscribers in South Amer-

ica the same as our domestic rate, that is \$5.00. We have been charging \$5.50. We find this postal rate no more expensive than that for North America.

For the present year we have a subscription list numbering 544 domestic subscribers and 216 foreign subscribers, making a total of 760. And there are 22 additional numbers mailed in the way of exchanges and complimentary copies, which makes the actual mailing list for the present year 782. I should also like to call attention to the number of pages devoted to the Contributed Papers section. In *The Journal* for 1932 there were 112 pages of contributed articles, and this year, 1933, we have practically doubled that number, devoting 225 pages to contributed articles. We have also attempted to classify the subject matter of these contributed papers, and that may be a matter of interest on account of the diversified activities of our members. There were 13 papers on foods and feeds, 6 on fertilizers, 2 on drugs, 1 on insecticides, and 18 papers on miscellaneous items, for example selenium, arsenic, fluorine and nitrogen.

It was also decided by the Committee that the names of the officers should appear in each number of *The Journal*.

F. C. BLANCK

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#### REPORT OF EDITORIAL COMMITTEE OF METHODS OF ANALYSIS

Work on the next revision of *Methods of Analysis* should begin after the 1934 meeting, and changes made at the 1935 should be included.

Referees, and associate referees if necessary, should be appointed without delay to compile material for the following chapters, which are included in the present edition by name only: Sewage, agricultural dust, fibers, paper, and paper materials, fish and other marine products, nuts and nut products, and vitamins. Other current topics, as for example, brewing and distillery raw materials and hops, should be considered.

The advisability of incorporating other tables and special and short-cut methods should also be carefully considered before active work is started on the 1935 edition. The method for the recovery of platinum from platinum waste is one that has come to the attention of the Committee recently.

J. A. LE CLERC

#### REPORT OF EDITORIAL COMMITTEE OF "PRINCIPLES AND PRACTICE OF AGRICULTURAL ANALYSIS"

Since the last meeting the Association has sold 26 copies of the new edition of Vol. II of Wiley's "Principles and Practice of Agricultural Analysis." The sales during the previous year were 23 copies. Fourteen copies of the volume have been given to the authors of chapters and reviews, so that there is now on hand 31 unsold copies out of the original

100 copies which were purchased from the Chemical Publishing Company in November, 1931. The sales of the book, even among the members of the Association, are disappointing, and do not offer much encouragement for the continuance of the original plan of publishing analytical works that are supplementary to *Methods of Analysis*, which notwithstanding the financial depression has continued to enjoy a good sale.

Notwithstanding frequent requests we have been unable to obtain from the Chemical Publishing Company of Easton, Pennsylvania, a statement of the sales, which they have made, of the published volume on "Fertilizers and Insecticides." Since the agreement was entered into by the Association with the Chemical Publishing Company and Dr. Wiley regarding the publication of the revision of "Principles and Practice," the passing of Dr. Wiley and the death of Mr. Knoll and Dr. Hart of the Chemical Publishing Company have entirely changed the situation with regard to our publishing the third volume of "Principles and Practice" upon foods, beverages and drugs. Because of the neglect of the present managers of the Chemical Publishing Company to push the sales of Volume II, it is the opinion of the committee that other arrangements should be made for the publication, under a different name, of the manuscripts of the chapters originally intended to form a part of Vol. III of "Principles and Practice." This, perhaps, may best be achieved, if it is decided to issue the work, by the Association's publishing separate monographs upon foods, beverages and drugs. As stated in the report of last year, manuscripts of twenty-two of the contemplated thirty-six chapters have been submitted. These chapters, before publishing, should be brought up to date.

The questions involved regarding the unsettled status of the volume already published, on "Fertilizers and Insecticides," and the future publication of the chapters on foods, beverages and drugs are now being carefully considered by the committee. This situation, which has been brought about by unforeseen circumstances, is another evidence of the present unsettled condition of the times.

It is hoped that at our next meeting a more definite and optimistic report upon the subject may be forthcoming.

C. A. BROWNE

Approved.

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#### REPORT OF COMMITTEE ON QUARTZ PLATE STANDARDIZATION AND NORMAL WEIGHT

In the absence of Mr. Bates I would state that Dr. Zerban, Mr. Bates and myself met and carefully considered this question and decided to submit no definite report at this time. The error in the scale of saccharimeters which was established some 20 years ago by Mr. Bates has since been

confirmed by Zerban of the New York Sugar Trade Laboratory, and by Balch and Hill, and so there is no question about the existence of that error. That error is counterbalanced by another error due to the volume of lead precipitate. We know what it is, as it has been carefully worked out by Zerban, for raw sugars. But the products our Association examines do not concern raw sugars, but mostly jams, jellies, etc., and we know nothing of the extent of the lead precipitate error for products of that kind. We have decided to hold our report in abeyance until these compensating errors can be determined. All we are recommending is a continuance of the present *status quo*. We simply recommend that the adaptability of Horne's dry subacetate of lead method of clarification to the polarization of jams, jellies, honeys, sirups and other food products be investigated by next year's Referee on Sugar with reference to the correction of the compensative volume of precipitate error in our present methods of polarization.

C. A. BROWNE

Approved.

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## REPORT OF COMMITTEE ON DEFINITIONS OF TERMS AND INTERPRETATIONS OF RESULTS ON FERTILIZERS AND LIMING MATERIALS

### *Final Adoption as Official*

#### 1. PHOSPHATE ROCK

*Phosphate rock* is a natural rock containing one or more calcium phosphate minerals of sufficient purity and quantity as to permit its use, either directly or after concentration, in the manufacture of commercial products.

#### 2. SOFT PHOSPHATE WITH COLLOIDAL CLAY

*Soft phosphate with colloidal clay* is a very finely divided low-analysis by-product from mining Florida rock phosphate by a hydraulic process in which the colloidal material settles at points in artificial ponds and basins farthest from the washer, and is later removed after the natural evaporation of the water.

#### 3. PRECIPITATED BONE PHOSPHATE

*Precipitated bone phosphate* is a by-product from the manufacture of glue from bones and is obtained by neutralizing the hydrochloric acid solution of processed bone with calcium hydroxide. The phosphoric acid is chiefly present as dicalcium phosphate.

#### 4. PRECIPITATED PHOSPHATE

*Precipitated phosphate* is a product consisting mainly of dicalcium phosphate obtained by neutralizing with calcium hydroxide the acid solution of either phosphate rock or processed bone.

### *Second Reading as Tentative*

#### 1. HIGH CALCIC PRODUCTS

*High calcic products* are materials 90 per cent or more of whose total calcium and magnesium content consists of calcium.

## 2. HIGH MAGNESIC PRODUCTS

*High magnesian products* are materials more than 10 per cent of whose total calcium and magnesium content consists of magnesium.

## 3. "BASIC" LIME PHOSPHATE (LIME BASED SUPERPHOSPHATE)

"Basic" lime phosphate (lime based superphosphate) is a superphosphate to which liming materials have been added in a quantity at least six per cent (6%) calcium carbonate equivalents in excess of the quantity required to convert all water-soluble phosphate to the citrate-soluble form.

## 4. LIME

The word *lime* when applied to liming materials means either calcium oxide or calcium and magnesium oxides.

## 5. MONO-AMMONIUM PHOSPHATE (FERTILIZER GRADE)

*Mono-ammonium phosphate (fertilizer grade)* is a commercial salt made by combining phosphoric acid with ammonia. It shall contain not less than ten per cent (10%) of nitrogen and not less than forty-six per cent (46%) of available phosphoric acid.

## 6. PHOSPHORIC ACID

The term *phosphoric acid* designates phosphoric oxide ( $P_2O_5$ ).

## 7. POTASH

The term *potash* designates potassium oxide ( $K_2O$ ).

## 8. UNIFORMITY IN USE OF TERMS "PHOSPHORIC ACID" AND "POTASH"

As the terms *phosphoric acid* and *potash* are used universally in guaranteeing and in reporting the analyses of fertilizers it is recommended that the same terms also be used in reporting and discussing the results of analyses of related materials.

## *Correction of Definition of "Superphosphate"*

The committee recommends that the definition of *superphosphate* printed in *Methods of Analysis*, A.O.A.C., 1930 be corrected to conform with the definition officially adopted, with some slight editorial changes, as follows: *Superphosphate* is the cured product obtained by mixing rock phosphate with sulfuric or phosphoric acid or with both.

## *First Reading as Tentative*

### 1. MANGANESE

The committee recommends that the water-soluble or available manganese in fertilizers be expressed as manganese (Mn).

### 2. MANGANESE SULFATE

The term *manganese sulfate*, when applied to an ingredient of a mixed fertilizer, shall designate anhydrous manganous sulfate ( $MnSO_4$ ).

### 3. CYANAMID

*Cyanamid* is a commercial product composed chiefly of calcium cyanamid ( $CaCN_2$ ), obtained by combining lime and carbon with nitrogen, and it shall contain not less than twenty-one per cent (21%) of nitrogen.

## *For Further Consideration*

Revision of official definitions for air-slaked lime, ground limestone, ground shell lime, and marl, ground shell marl.



G. S. FRAPS, <i>Acting Chairman</i>	L. E. BOPST
H. D. HASKINS, <i>Chairman</i>	L. S. WALKER (for C. H. JONES)
J. W. KELLOGG	W. H. MACINTIRE

Approved.

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## REPORT OF COMMITTEE ON RECOMMENDATIONS OF REFEREES

The work of the Association of Official Agricultural Chemists is primarily devoted to the development of methods of analysis. This work is carried on by referees, associate referees and collaborators, aided by various committees. The system is as old as the Association itself, and it is only for the benefit of newer members that duties and essentials of procedure need occasionally to be reviewed.

*Referees and Associate Referees.*—The duties of referees and associate referees are defined in the constitution. These officers are (1) to direct and conduct research on methods and subjects assigned to them; (2) to prepare and distribute samples and reagents to collaborators; (3) to present at the annual meeting of the Association the results of work done and recommendations of methods based thereon; and (4) to direct and encourage general discussion at the meeting.

A referee is appointed to study a given subject or a general group of subjects. In the latter case associate referees are appointed to assist him by taking over consideration and study of subdivisions of the general group. Referees and associates should review work and recommendations made in connection with their assignments as shown by the proceedings of the Association for the previous year, or earlier years, in order that they may have a clear picture of what has been done, avoid needless repetition of work, and better determine what work should be undertaken. They will, of course, keep informed on chemical and other scientific literature and be alert for suggestions that may lead to new methods of value or to improvements in present methods.

When preliminary studies on the part of referees and associate referees suggest new methods or changes in present methods, the procedures will be submitted to collaborative study. Methods may work well in the hands of the originators, but they may not work so well in the hands of chemists not familiar or experienced with them. Procedures should, therefore, be carefully detailed and clearly stated when submitted for collaborative study. It sometimes happens that description of a method may appear to the author to be entirely adequate, yet it may omit essential details that he observes but which will not be obvious to others. Referees and associates should submit samples and directions to collaborators as early in the year as possible to insure early reports from them.

Collaborators should be advised to submit to referees and associate referees all their results except, of course, such as are known to be in error.

In some cases it may be advisable for collaborators to try the method submitted to them on unofficial material before applying it to official samples submitted by the referees. Reasonable skill and accuracy on the part of collaborators is assumed; but the purpose of collaborative work is the trial of methods, not of analysts. Selected results favorable to methods under study may defeat the purpose sought.

Methods to be adopted as official, or changes to be made in official methods, must be recommended by the referee for such action at two annual, but not necessarily consecutive, meetings of the Association. Final action on adoption does not follow first action automatically; the referee must recommend the second (final) action.

Methods to be adopted as tentative require only one recommendation on the part of the referee and publication of the methods in the proceedings of the Association.

Departures from this regular method of procedure for the adoption of methods can only be made by vote of the active members of the Association to suspend the by-laws involved.

*Preparation of Reports.*—In summarizing work for report to the Association referees and associate referees should make known their own appraisal of the data obtained in the form of definite recommendations. Thus recommendations may be made for *further study* in case the work has not developed to the point where recommendation for adoption of methods is warranted; or recommendations may be made for adoption of procedures as *tentative methods* in case the procedures so recommended have not the degree of accuracy or reliability expected of an official method but are, nevertheless, sufficiently accurate for the purpose intended, or are the best methods at present available; and finally recommendations may be made for adoption of methods as official, specifying *first action* if that is the case, or *final action* if first action has already been taken at some previous meeting.

In case referees have not covered in the current year all recommendations that have been made on their subjects they should renew such old recommendations in their reports for the current year. It is, however, within the province of referees and associate referees to recommend discontinuance of such previous recommendations if the studies contemplated seem likely to serve no urgent need or useful purpose. Reasons for such recommendations should be included in the text of the report. It is needless to point out that referees may, and are expected to, recommend new studies of methods pertinent to the work of the Association.

Approved forms of recommendations just discussed are as follows:

It is recommended—

(1) That study of methods for the determination of — in — be continued (or discontinued) during the coming year.

(2) That the method described in this report (or as given in Vol. — p. — year — of the Proceedings) be adopted as a tentative method.

(3) That the method described in this report (or as given in Vol. — p. — year — of the Proceedings) be adopted as an official method, first action.

(4) That the method described in this report (or as given in Vol. — p. — year — of the Proceedings) be adopted as an official method, final action. (First action taken in year —.)

(5) That the official method for the determination of — (give reference to *Methods of Analysis*) be revised to read — (give exact language of proposed change). This is a recommendation for a change in an official method, first action.

(6) That the official method for the determination of — (give reference to *Methods of Analysis*) be revised to read — (give exact language of proposed change). This is a recommendation for a change in an official method, final action. (First action taken in year —.)

NOTE.—Forms 5 and 6 may be adapted to a recommendation for the deletion of an official method. Two actions are necessary.

(7) That studies of methods for the determination of — in — be undertaken.

*Presentation of reports.*—In presenting reports to the convention the purpose and plan of the work and the results accomplished should be clearly stated. It is desirable, especially in the case of long reports, to summarize somewhat, but enough detail should be given to permit comment and discussion. Lengthy recitals of numerical values, detailed accounts of analytical procedure and minute descriptions of apparatus are not likely to be followed by the audience. The use of slides for such purposes is helpful and is recommended. There can be no fixed rule in the matter of presentation of reports, and the good judgment of the person making the report will decide his course. Above all, referees and others making reports should feel that there is no disposition to curtail an adequate exposition of their work.

In addition to this summary of some of the essential features of the mechanism provided for carrying on the development of methods of analysis, the Committee expresses its appreciation of the splendid co-operation given by the staff of referees, associate referees and their collaborators. The Association is indebted to them all for their loyal support in these difficult times.

E. M. BAILEY, *Chairman*

Approved.

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## REPORT OF SUBCOMMITTEE A ON RECOMMENDATIONS OF REFEREES

By H. H. HANSON (State Board of Agriculture, Dover, Delaware), *Chairman*; H. R. KRAYBILL and G. L. BIDWELL

The following recommendations submitted by Subcommittee A were approved by the Association unless otherwise stated.

## INSECTICIDES, FUNGICIDES AND CAUSTIC POISONS

It is recommended—

(1) That Method II for the determination of lead oxide and copper in Bordeaux-lead arsenate mixtures [*This Journal*, 15, 289 (1932); 16, 69 (1933)] be adopted as official (final action).

(2) That the Willard-Winter method for the determination of fluorine (*This Journal*, 16, 105 (1933) and *Ind. Eng. Chem. Anal. Ed.*, 5, 7 (1933)] be adopted as a tentative method.

(3) That further study be made of the recovery of fluorine from plant ash.

## SUGARS AND SUGAR PRODUCTS

It is recommended—

(1) That the adaptability to the polarization of jams, jellies, honeys, sirups, and other food products of Horne's dry subacetate of lead method of clarification [*Methods of Analysis*, A.O.A.C., 1930, 368, sec. 18 (c)] be investigated with reference to the correction of the compensating volume of precipitate error in the present methods of polarization of the Association.

(2) That the Gothe method<sup>1</sup> for the determination of diastase in honey be studied.

(3) That the studies on honey recommended last year be continued.

(4) That the sentence "To facilitate the filtration a hot water funnel, suction, or a 'filter-aid' may be employed" in the tentative method for the preparation of sample under maple products [*Methods of Analysis*, A.O.A.C., 1930, 391, sec. 103 (a), par. 2] be deleted.

(5) That the method for preparation of sample under maple products, as amended, be adopted as official (first action).

(6) That the directions for preparing the reagent used in the determination of the Winton lead number, changed last year and made official, first action [*This Journal*, 16, 80 (1933)], be made official (final action).

(7) That the directions for preparing the reagent used in the determination of the Canadian lead number (Fowler modification), changed last year and made official, first action [*This Journal*, 16, 80 (1933)], be made official (final action).

(8) That the directions for determining conductivity value, official, first action [*Methods of Analysis*, A.O.A.C., 1930, 393], as revised last year, first action [*This Journal*, 16, 80, (1933)], be made official (final action).

(9) That data be accumulated to establish the range of the lead values obtained in genuine maple products by the reagents in the Winton and Canadian lead value methods.

(10) That to the official method for determining moisture in maple sirup (*Methods of Analysis*, A.O.A.C., 1930, 391, par. 104) the following sentence be added: "In the refractometric measurement guard against

<sup>1</sup> *Z. Unters. Nahr-Genussm.*, 28, 286 (1914).

deposition of dew on the prisms by circulating water of room temperature through the prism jackets and correcting the observations to 20° by use of Table 7, p. 512 (*Methods of Analysis, A.O.A.C.*, 1930), (official, final action).

(11) That the directions for the official polarimetric determination of sucrose in maple products (*Methods of Analysis, A.O.A.C.*, 1930, 392, par. 107) be changed to read: "Calculate the results of 105, using the appropriate formula from 22 or 23 (official, final action).

(12) That the changes in the official directions for preparation and use of clarifying reagents adopted last year under Nos. (1), (2), (3), and (4), [*This Journal*, 16, 78-9 (1933)], as official, first action, be adopted as official, final action.

(13) That the amendment to the official refractometric method for the determination of solids in maple products (*Methods of Analysis, A.O.A.C.*, 1930, 365, par. 7), adopted as official (first action) last year [*This Journal*, 16, 81 (1933)], be adopted as official, final action.

(14) That the method of Rice and Boleracki<sup>1</sup> for the determination of moisture in sirups be further studied.

(15) That the new single-prism refractometer described by Landt<sup>2</sup> be further investigated.

(16) That study on polariscopic methods be continued along the lines covered by the recommendations made and approved in 1931 and 1932 [*This Journal*, 14, 43 (1932)].

(17) That paragraphs 32 and 33 of Chapter XXXIV (*Methods of Analysis, A.O.A.C.*, 1930, p. 377) be deleted.

(18) That paragraph 44 of Chapter XXXIV (*Methods of Analysis, A.O.A.C.*, 1930, p. 381) be deleted (first action).

(19) That paragraphs 55 and 56 of Chapter XXXIV (*Methods of Analysis, A.O.A.C.*, 1930, p. 384) be deleted (first action).

#### FEEDING STUFFS

It is recommended—

(1) That the following recommendation, approved in 1931 and again in 1932, be continued: "That the methods of preparation of solution and determination of sugars in feeding stuffs (*Methods of Analysis, A.O.A.C.*, 1930, 281), adopted as official (first action) in 1930, be further studied.

(2) That an associate referee be appointed to study these and other methods in regard to their adaptability to feeding stuffs.

(3) That the title "Biological Methods for Determining Cod Liver Oil in Feed Mixtures" be changed to read "Biological Methods for Vitamin Carriers (Feeding)."

(4) That an associate referee be appointed to study biological methods for vitamin B complexes.

<sup>1</sup> *Ind. Eng. Chem. Anal. Ed.*, 5, 11 (1933).

<sup>2</sup> *Z. Ver. deut. Zucker-Ind.*, 83, 692 (1933).

(5) That an associate referee be appointed to study the technic and details involved in the biological methods of assay of vitamin D carriers from the time of killing the chicks to the completion of the ash determination.

(6) That an associate referee be appointed to study the mechanical method of separation, as outlined by the Bureau of Agricultural Economics, for the classification of alfalfa products.

(7) That the subject of fluorine in feeds be investigated and that the subject be referred to the associate referee on this subject in the food section.

(8) That further study be given to the microanalytical detection of iodine in feeding stuffs.

(9) That a study be made of methods for the detection of mineral adulterants in feeding stuffs.

(10) That the Knapheide and Lamb method for the determination of iodine in mineral mixed feeds<sup>1</sup> be adopted as tentative (see p. 67).

(11) That the study of the Knapheide-Lamb method and other methods for the determination of iodine be continued.

(12) That studies of methods for the determination of lime (calcium oxide) in mineral mixed feeds be continued.

(13) That the official method for determining moisture in grain and stock feeds (*Methods of Analysis*, A.O.A.C., 1930, 277, sec. 2) be changed by striking out the words: "at the temperature of boiling H<sub>2</sub>O" in the first line and substituting therefor the words: "at a temperature of 95°-100° C." (first action).

(14) That in the same method (p. 277, sec. 2) the provision for drying in a current of H be deleted (first action).

(15) That in the same method for determining moisture and in the electric air-oven method (p. 278), the use of covered aluminum dishes at least 50 mm. in diameter and not exceeding 40 mm. deep be specified (first action).

(16) That the method of vitamin D assay recommended by the associate referee be adopted as tentative (see p. 69).

(17) That the method be subjected to further study, collaboratively, if it is considered feasible by the associate referee.

(18) That the biological detection of vitamin D carriers in mixed feeds be studied.

(19) That the Alkaline Titration Method-Tentative (*Methods of Analysis*, A.O.A.C., 1930, 287, 38) be deleted.

(20) That the acid titration method, the Prussian blue methods, and the gravimetric method described by the associate referee this year be further studied.

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<sup>1</sup> *J. Am. Chem. Soc.*, 50, 2121 (1928).

(21) That in the last sentence of the Prussian blue method (*Methods of Analysis*, A.O.A.C., 1930, 287, par. 39) the words "from a standard soln containing 1 mg of KCN diluted to 25 cc" be changed to read, "from the vacuum evaporation of a standard solution containing 1 mg. of KCN diluted to 25 cc," and that the following sentence be added: This solution, containing 1 mg of KCN, = 0.415 mg of HCN.

(22) That further study be given to dichloromethane as a fat solvent.

(23) That further study be made of the Goldfish extraction apparatus and the modifications given in the report of the associate referee.

(24) That a more detailed study of the work outlined by the Associate Referee on Fats in Dairy Products Used as Feeds be made.

#### SOILS AND LIMING MATERIALS

It is recommended—

(1) That the methods of analysis adapted to the soils of the arid and semi-arid region presented in the report of P. L. Hibbard be further studied.

(2) That the methods of procedure for the chromic acid, or "wet combustion," method for the determination of organic matter in soils described in the paper of J. W. White be further studied with a view to the possibility of incorporation in the next revision of *Methods of Analysis*.

(3) That the work on the reaction value of acid soils be continued.

(4) That the recommendations adopted last year on less common metals in soils be continued [(*This Journal*, 16, 43 (1933)).

#### FERTILIZERS

It is recommended—

(1) That the subject of methods for the determination of manganese and magnesium and the equivalent acidity or basicity of fertilizers be referred to the Associate Referee on High Analysis Fertilizers for study.

(2) That a collaborative study be made of the determination of free acid in superphosphates.

(3) That the first of the alternative methods for preparing ammonium citrate solution [*Methods of Analysis*, A.O.A.C., 1930, 17, sec. 13 (1)] be deleted (final action). This involves also deletion of the preceding sentence, "prepare according to either," etc. . . .

(4) That the second method for the preparation of ammonium citrate solution, published previously [*This Journal*, 16, 68 (1933)], be adopted as official (final action).

(5) That the study of the use of the catalysts selenium and mercury in the determination of total nitrogen in fertilizer materials and mixed fertilizers be discontinued.

(6) That further study be made of the methods for determining water-insoluble nitrogen in cyanamid.

(7) That the official volumetric method for determining water-soluble phosphoric acid (*Methods of Analysis*, A.O.A.C., 1930, 17, 12) be amended by inserting "0.1" between the word "to" and the figure "0.2" in the second line, so that the sentence will read: "To an aliquot of the soln corresponding to 0.1, 0.2 or 0.4 g," etc. (first action).

(8) That collaborative work be conducted on the determination of moisture in hygroscopic fertilizer salts and mixtures by the official method specifying distillation with toluene (*Methods of Analysis*, A.O.A.C., 1930, 277).

(9) That a study be made of the recommendation of the associate referee that the following phrase be inserted in line 7 after the word "crucible" of the official method for the determination of potash in mixed fertilizers [*Methods of Analysis*, A.O.A.C., 1930, 26, sec. 43 (a)]: "(Prepared with an acid-washed asbestos pad of such thickness that under a slight suction hot water will be drawn through in a series of rapid drops)."

(10) That study be made of the recommendation of the associate referee that the last two sentences in section 43 (a), p. 26, *Methods of Analysis*, A.O.A.C., 1930, be changed to read as follows: "Weigh and remove the chloroplatinate precipitate by washing with hot water, using slight suction. Wash with 80 per cent alcohol three times, dry as before, and weigh. (Loss equals  $K_2PtCl_6$ .) Calculate to  $K_2O$ ."

(11) That collaborative study be made of the losses resulting when the official method for the determination of potash is used on pure potassium salts alone, and in the presence of the usual accompanying salts.

(12) That comparative studies be made of the use of 80 per cent alcohol for washing when saturated with  $K_2PtCl_6$  and as directed by the official method.

#### PLANTS

It is recommended—

(1) That the associate referees continue their studies of the methods for making the following determinations on plant materials: Forms of nitrogen, less common elements, chlorine, sodium and potassium, and carbohydrates.

(2) That methods for the determination of fluorine in plants be further studied in cooperation with associate referees in other sections who are interested in the determination of this element.

(3) That study be continued on the less common metals in plants.

(4) That the study of the Christy-Robson method for the determination of chlorine in plant materials be continued.

(5) That study of carbohydrates in plants be continued.

(6) That the method for the determination of nitrate nitrogen in tobacco described in the report of the associate referee be adopted as tentative. The method has been published [*This Journal*, 16, 474 (1933)].



(7) That the study of methods for the determination of sodium in plants be continued.

(8) That the perchlorate method for the determination of potassium in plant materials be studied.

#### LIGNIN

It is recommended that further work be done on the fuming hydrochloric acid method for the determination of lignin.

#### ENZYMES

It is recommended—

(1) That the peroxidase method be subjected to collaborative study with the purpose in view of adopting it as an official method.

(2) That the recommendation of last year in regard to catalase [*This Journal*, 16, 50 (1933)] be continued.

### REPORT OF SUBCOMMITTEE B ON RECOMMENDATIONS OF REFEREES

By L. E. WARREN (U. S. Food and Drug Administration, Washington, D.C.), *Acting Chairman*; A. G. MURRAY  
and L. B. BROUGHTON

The following recommendations submitted by Subcommittee B were approved by the Association unless otherwise stated.

#### NAVAL STORES

No collaborative work was done. It is recommended that the subject be continued.

No collaborative work was done on turpentine. It is recommended that the topic be continued.

#### PAINTS, PAINT MATERIALS AND VARNISHES

No collaborative work was done. It is recommended that the subject be continued.

#### BEERS, WINES AND DISTILLED LIQUORS

No collaborative work was done. It is recommended that the topic be continued.

#### DRUGS

##### CRUDE DRUGS

The roots of *Aconitum napellus*, var. *firmum*, were studied from the pharmacognostical standpoint and methods of identification developed.

It is recommended—

(1) That further work on this subject be done.

(2) That psyllium seed be also considered during the coming year.

## RADIOACTIVITY IN FOODS AND DRUGS

No work was done this year. It is recommended that the topic be continued.

## CALCIUM GLUCONATE

It is recommended that the method for the determination of the gluconate ion as published [*This Journal*, 15, 465 (1932)] be adopted as tentative after incorporation of the changes suggested by the associate referee (see p. 75).

## MERCURIALS

Mercurochrome was studied as a type of mercury containing dyes.

It is recommended—

(1) That the tests for purity of mercurochrome described by the associate referee be adopted as tentative (see p. 75).

(2) That the method for the determination of total solids described by the associate referee be adopted as tentative (see p. 75).

(3) That the method for the determination of mercury in mercurochrome described by the associate referee be adopted as tentative (see p. 76).

## MICROCHEMICAL METHODS FOR ALKALOIDS

This topic has been continued over several years with additions and closures each year. The work this year covered papaverine and procaine.

It is recommended—

(1) That the microchemical methods for the identification of papaverine described by the associate referee be adopted as tentative (see p. 76).

(2) That the microchemical methods for the identification of procaine described by the associate referee be adopted as tentative (see p. 76).

(3) That the subject be continued with special reference to scopolamine, hyoscyamine, homatropine and atropine.

## MICROCHEMICAL METHODS FOR SYNTHETICS

Amidopyrine, antipyrine, methenamine and triethanolamine were studied.

It is recommended—

(1) That the microchemical methods for the determination of antipyrine, methanamine and triethanolamine described by the associate referee be adopted as tentative (see p. 77).

(2) That further study be made of amidopyrine.

(3) That phenacetin, acetanilid, and barbitol and its derivatives be studied during the coming year.

## HYPOPHOSPHITES

Considerable work was done on this topic but the problem was not completed. It is recommended that the subject be continued.

## SANTONIN

No report was submitted. It is recommended that the topic be reassigned.

## ETHER

This subject involves the determination of ether in mixtures. Considerable progress was made. It is recommended—

- (1) That the method proposed last year by the associate referee be adopted as tentative [*This Journal* 16, 357, (1933)].
- (2) That the title of the method be followed by the phrase "Not applicable in the presence of essential oils."
- (3) That the subject be closed.

## BENZYL COMPOUNDS

The method studied gave promising results. It is recommended that the subject be continued.

## SMALL QUANTITIES OF MORPHINE IN SIRUPS

Considerable progress was made on this new topic. It is recommended that further work be done.

## GUAIACOL

No report was submitted. It is recommended that the subject be reassigned.

## BROMIDE-BROMATE VOLUMETRIC SOLUTIONS

It is recommended—

- (1) That the changes recommended by the associate referee for the purpose of unification be made in the official methods (see p. 78).
- (2) That the topic be closed.

## RHUBARB AND RHAPONTICUM

Considerable work in testing the laxative properties of these drugs on the daphnia was reported.

It is recommended that the topic be continued.

## TETRACHLORETHYLENE

A method of assay developed converts the tetrachlorethylene into chloride, which is then determined either gravimetrically or volumetrically.

It is recommended—

- (1) That the method submitted by the associate referee be adopted as tentative (see p. 78).
- (2) That studies be undertaken to determine tetrachlorethylene in mixtures.

## HEXYLRESORCINOL

No report was received. It is recommended that the topic be again assigned.

**ERGOT ALKALOIDS**

Considerable progress was reported, but the study is not completed. It is recommended that the subject be continued.

**BIOLOGICAL TESTING**

No report was received. It is recommended that the topic be reassigned.

**NITRITES IN TABLETS**

The associate referee studied several methods, but they were not submitted to collaborative tests. The chlorate method was found to be best. It is recommended that collaborative work be done with this method.

**OINTMENTS**

Iodine ointment was selected for study, and several methods for its assay were tested by the associate referee. No collaborative work was carried out. It is recommended that the subject be studied further.

**ACETPHENETIDIN IN PRESENCE OF CAFFEINE AND ASPIRIN**

The Association has adopted methods for the determination of acetylsalicylic acid in the presence of caffeine and acetphenetidin, but it has no method for the determination of acetphenetidin in the presence of caffeine and aspirin. A method was developed by the associate referee and submitted for collaborative study. The results are not so uniform as desired.

It is recommended that the topic be continued.

**STRYCHNINE IN TABLETS**

The associate referee made no report. The Referee on Drugs has made suggestions for preparing coated and uncoated tablets, tablet triturates and pills containing strychnine for analysis.

It is recommended—

(1) That these directions for preparation of sample (see p. 79) be adopted as official (first action).

(2) That the topic be closed.

**PYRIDIUM**

A preliminary report was submitted. It is recommended that the topic be continued.

**GUMS**

The associate referee developed some interesting methods for the identification of single gums.

It is recommended that the topic be continued with special reference to the identification of gums in mixtures.

**ESSENTIAL OILS**

The associate referee made a study of the literature. Some work was

done on the assay of lemon oil for citral but no collaborative tests were carried out.

It is recommended that the topic be continued.

#### RESINS AND OLEORESINS

Two samples of podophyllum were sent to collaborators to be assayed for resin by a method suggested by the associate referee. No reports were received. It is recommended that the topic be continued.

### REPORT OF SUBCOMMITTEE C ON RECOMMENDATIONS OF REFEREES

By H. A. LEPPER (U. S. Food and Drug Administration, Washington, D.C.), *Acting Chairman*; G. G. FRARY and J. O. CLARK<sup>1</sup>

The following recommendations submitted by Subcommittee C were approved by the Association unless otherwise stated.

#### EGGS AND EGG PRODUCTS

It is recommended that the studies on the following methods be continued, as detailed last year [*This Journal*, 16, 55 (1933)]: Total phosphoric acid ( $P_2O_5$ ), fat (acid hydrolysis), lipoids and lipid  $P_2O_5$ , reducing sugars and sucrose, crude albumin nitrogen, chlorine, unsaponifiable matter, glycerol (qualitative and quantitative), acid-soluble  $P_2O_5$ , ammonia nitrogen, and acidity of ether extract.

#### FOOD PRESERVATIVES

It is recommended—

(1) That the method for the determination of saccharine proposed by the referee be further studied to determine its suitability for adoption as official to replace the present official method.

(2) That the Monier-Williams method for the determination of total sulfurous acid be made official (first action).

(3) That the official methods for the determination of sulfurous acid (*Methods of Analysis*, A.O.A.C., 1930, 343-4, 31, 32) be dropped (first action).

(4) That line 6 of the qualitative test for sulfurous acid (*Methods of Analysis*, A.O.A.C., 1930, 343, 30) be changed to provide verification of positive results by the Monier-Williams method (first action).

(5) That the change in the official quantitative method for the determination of boric acid (*Methods of Analysis*, A.O.A.C., 1930, 340, 16) providing for the use of 1 to 2 grams of mannitol instead of 10 grams for the titration be made (final action).

<sup>1</sup> In the absence of Mr. Frary and Mr. Clark, E. M. Bailey and W. B. White served on the committee.

## COLORING MATTERS IN FOODS

It is recommended—

(1) That additional collaborative work be devoted to the separation and identification of coloring matters in macaroni products.

(2) That the study of the quantitative separation of ponceau S X and sunset yellow from the other permitted dyes be continued.

(3) That additional investigational work be devoted to the qualitative separation of light green S F yellowish, fast green F C F and brilliant blue F C F.

## METALS IN FOODS

It is recommended—

(1) That the bromate method for the determination of arsenic on fresh fruit, made tentative last year [*This Journal*, 16, 75 (1933)], be amended by substituting hydrazine sulfate for ferrous sulfate for reduction purposes so as to facilitate the determination of lead in the residue.

(2) That the bromate method be restricted to the determination of arsenic in fruits or vegetables where a sample containing at least 0.005 grain or 0.3 mg. of  $\text{As}_2\text{O}_3$  can be digested.

(3) That no further work be done on the bromate method for the determination of arsenic.

(4) That study of the arsine distillation method for the determination of arsenic be continued.

(5) That study of the Gutzeit method from the points of view of technic and interfering substances be continued.

(6) That colorimetric methods for the determination of quantities of copper up to 1 mg. and macro and micro quantities of zinc, with the dividing line at approximately 2 mg., be studied.

(7) That study of methods for the detection of fluorine be continued, with especial attention given to the preparatory treatment of organic material.

(8) That methods for the determination of lead be studied collaboratively.

## FRUITS AND FRUIT PRODUCTS

It is recommended—

(1) That study of methods for the determination of constituents of the ash be discontinued.

(2) That study on the analysis of fruit products by a method of adjusted hydrogen-ion concentration be discontinued.

(3) That study of the refractometric method for the determination of soluble solids be continued.

(4) That the method for the determination of *l*-malic acid published by Hartmann and Hillig [*This Journal*, 15, 648 (1932)] be adopted as tentative.

(5) That the method for the determination of inactive malic acid pub-

lished by Hartmann and Hillig [*This Journal*, 16, 277 (1933)] be studied collaboratively.

(6) That study of methods for the determination of lactic acid be continued.

(7) That the tentative method for the determination of pectic acid be studied.

(8) That electrometric methods for titrating fruits and fruit products be studied.

(9) That study of the changes in the character of sugar when dried in the presence of acids be continued.

(10) That the official methods for the determination of moisture in dried fruits (*Methods of Analysis*, A.O.A.C., 1930, 264, 3) be revised (first action) to substitute "6 hours" for "12 hours" in line 3.

(11) That the tentative method for the determination of moisture in dried apples (*Methods of Analysis*, A.O.A.C., 1930, 265, 4) be dropped.

(12) That the method of sampling boxed dried fruits presented by the associate referee be adopted as tentative.

#### CANNED FOODS

It is recommended—

(1) That studies of methods for determining quality factors and fill of container be continued.

(2) That studies of methods for solids in tomato products be continued.

#### DAIRY PRODUCTS

It is recommended—

(1) That the official optical method for the determination of lactose in milk (*Methods of Analysis*, A.O.A.C., 1930, 216) be studied to correct an apparent error pointed out by the referee.

(2) That the determination of fat in malted milk by the method proposed by the associate referee be studied collaboratively and that further work be done on the determination of the Reichert-Meissl value on fat as extracted.

(3) That no further work be undertaken on the recommendation pertaining to the determination of the Reichert-Meissl value by the method previously proposed [*This Journal*, 16, 60 (1933)].

(4) That study of the determination of milk solids in malted milk by means of a citric acid determination be dropped.

(5) That the recommendation for the determination of casein in malted milk approved last year be repeated.

(6) That the mounting medium in the method for microscopical identification of malted milk (*Methods of Analysis*, A.O.A.C., 1930, 230) be studied.

(7) That work be continued on the determination of moisture in dried milk by the distillation method.

- (8) That work on methods of sampling be continued.
- (9) That studies on sampling tub, cube and print butter be continued.
- (10) That studies on the composition of the individual units in the churning be continued with a view to recommending a suitable sampling procedure to cover the unit package as well as the average unit in the churning or batch.
- (11) That the modified stirrer method outlined by the associate referee be further studied collaboratively.
- (12) That the methods for determining salt and curd (*Methods of Analysis, A.O.A.C.*, 1930, 237) be studied to determine the best method of removing last traces of fat.
- (13) That studies on methods for distinguishing sweet cream butter from neutralized butter be continued but that work on the other recommendations be given precedence.
- (14) That further collaborative study be given to the alundum-Gooch crucible method (*Methods of Analysis, A.O.A.C.*, 1930, 236, 77) for the determination of fat in butter.
- (15) That the tentative methods for the determination of citric and tartaric acids in cheese (*Methods of Analysis, A.O.A.C.*, 1930, 240, 241) be made official (final action).
- (16) That further work on the  $P_2O_5$ -CaO ratio be dropped.
- (17) That further collaborative work be done on the ash and salt content of cheese, the Volhard method to be used and checked against other standard methods.
- (18) That the work on added gums in cheese be carried on by the Referee on Gums in Foods.
- (19) That the associate referee study and report on the advisability of deleting the gravimetric method for the determination of fat (*Methods of Analysis, A.O.A.C.*, 1930, 239, 97).
- (20) That the Babcock centrifugal method for the determination of fat in ice cream be further studied.
- (21) That the methods for the determination of casein and albumin in milk, including those proposed by the associate referee, be further studied with a view to the adoption of not more than one for each protein, if possible.
- (22) That methods for the detection of gelatin in dairy products be studied.

#### CEREAL PRODUCTS

##### *Flour, Macaroni Products and Baked Products*

It is recommended—

- (1) That the title "Alimentary Pastes" (*Methods of Analysis, A.O.A.C.*, 1930, 180) be changed to "Macaroni Products."
- (2) That special (non-collaborative) studies be conducted on the meth-



ods for the determination of unsaponifiable matter in the fat of flour, baked products and macaroni products, formerly called alimentary pastes, in conjunction with the same study on eggs.

(3) That further study be made of the tentative method for the determination of crude albumin nitrogen in flour, macaroni products and baked products, in conjunction with similar methods for eggs.

(4) That comparative tests be made of foreign and domestic methods of chemical analysis used as measures of evaluating flour, macaroni and baked products.

(5) That  $\gamma$ (2:5) dinitrophenol ( $pH=4.0-5.6$ ) and paranitrophenol ( $pH=5.4-7.0$ ) be studied collaboratively in making colorimetric  $pH$  determinations on flour, bread and macaroni products, and that as a basic method the modification of the tentative method suggested by the associate referee be used.

(6) That further study be made of the method of ashing flour, macaroni products and baked products with the object of reducing the time of combustion.

(7) That the acid hydrolysis method for the determination of fat in macaroni and baked products be further studied.

(8) That the method modified by the associate referee last year for the determination of phosphorus in eggs be studied collaboratively in regard to its applicability to flour, macaroni and baked products.

(9) That the method modified by the associate referee last year for the determination of lipoids and lipid-phosphorus in flour, macaroni and baked products be further studied.

(10) That the methods for the determination of chlorine in bleached flour and the method of the associate referee for the determination of  $BzO_2$  as benzoic acid in bleached flour be further studied.

(11) That the method proposed by the associate referee for the determination of the diastatic power of flour be adopted as tentative.

(12) That the study of methods for the determination of color in flour be resumed, special attention being paid to the use of the Munsell or similar apparatus.

(13) That the present tentative method (*Methods of Analysis, A.O.A.C.*, 1930, 172) for the determination of starch be revised as outlined in the associate referee's report for 1932 [*This Journal*, 16, 504 (1933)] and the method be further studied.

(14) That the  $CHCl_3$  test for the detection of rye flour in wheat flour be adopted as tentative (see p. 65).

(15) That the  $CHCl_3$  test, the modified Tillmans method and the König-Bartschat method be further studied.

(15) That methods for the determination of carbon dioxide in self-rising flour be further studied.

(16) (a) That the vacuum oven method for the determination of

moisture in bread (*Methods of Analysis, A.O.A.C., 1930, 177, 48*) be adopted as an official method for this determination in all air-dried baked products not containing fruit (final action).

(b) That the 130°C. air oven method for the determination of moisture in bread (*Methods of Analysis, A.O.A.C., 1930, 177, 49*) be adopted as an official method for this determination in all air-dried baked products not containing fruit (final action).

(c) That methods for the determination of moisture in baked products containing fruit be further studied.

(17) That the official method for the determination of crude fiber in bread (*Methods of Analysis, A.O.A.C., 1930, 178, 55*) be adopted as official for this determination in all baked products (first action).

(18) That study be continued on methods to determine milk solids in bread.

(19) That the method for the determination of chlorides in flour and baked products be further studied.

(20) That the standard baking test be retained as tentative and that work on this subject be temporarily discontinued.

(21) That the method for the preparation of sample of macaroni products be retained as tentative and that work on this subject be temporarily discontinued.

(22) That methods for determining chlorides in baked products (official, first action) be further studied before final action is taken.

(23) That a study be made of the methods and of the viscosimeter best adapted for the determination of viscosity in flour-and-water-suspensions.

(24) That a study be made of the method for cold water-soluble extract of flour and at the same time of the possibility of using this extract for the determination of acidity in flour.

(25) That a study be made of the methods for the determination of ergot in wheat and in rye flour.

(26) That a study be made of the methods for the determination of catalase and proteolytic activity of flour.

#### BAKING POWDERS AND BAKING CHEMICALS

It is recommended—

(1) That direct methods for the determination of available carbon dioxide be studied for the purpose of limiting the methods to as few as possible.

(2) That studies of the tentative method for the determination of aluminum by its precipitation with phenylhydrazine be continued.

(3) That studies of methods for the determination of free phosphoric acid in calcium acid phosphate, as proposed by Cox or others, be continued.

## VINEGARS

It is recommended—

(1) That methods for the determination of total and soluble ash be further studied, with particular attention given to the use of sucrose or other substances for reducing the time of heating and to the temperature of ashing.

(2) That methods for the determination of phosphoric acid be further studied in connection with the studies on ash.

(3) That the official method for the determination of solids be studied, especially with reference to its application to vinegar high in solids, such as malt vinegar.

(4) That the official method for the determination of glycerol be revised (first action) to substitute the use of diphenylamine as an inside indicator for potassium ferricyanide as an outside indicator and to substitute the simplified method of calculation [*This Journal*, 15, 536 (1932)] for the present calculation (*Methods of Analysis*, A.O.A.C., 1930, 360, 63).

## FLAVORS AND NON-ALCOHOLIC BEVERAGES

It is recommended that methods for the determination of essential oil in extracts and toilet preparations be studied collaboratively.

## MEAT AND MEAT PRODUCTS

It is recommended—

(1) That the study of methods for the determination of nitrate and nitrite nitrogen in meat and meat products, including meat extracts and curing solutions, be continued.

(2) That the method adopted in 1932 as tentative for the determination of salt in meat be adopted as official (first action).

## GELATIN

It is recommended—

(1) That collaborative studies on the preparation of sample be continued.

(2) That the tentative method for the determination of arsenic, with the modification suggested by the referee in 1932 [*This Journal*, 16, 547 (1933)], be subjected to collaborative study and that the procedure be correlated with that of the official method (*Methods of Analysis*, A.O.A.C., 1930, 306) as closely as possible.

## SPICES AND OTHER CONDIMENTS

It is recommended—

(1) That the methods for the determination of volatile oils in spices and for specific gravity, optical rotation, refractive index, eugenol, and acid and ester numbers of the separated oil, given by the associate referee, be adopted as tentative and further studied (see p. 70).

(2) That the methods for the determination of total solids, acidity, nitrogen and  $P_2O_5$  in salad dressings published last year [*This Journal*, 16, 77, 78 (1933)] be adopted as official (final action).

(3) That studies of methods for starch and sugars in prepared mustard be temporarily discontinued.

#### CACAO PRODUCTS

It is recommended—

(1) That the present tentative method for the determination of casein in milk chocolate\* (*Methods of Analysis*, A.O.A.C., 1930, 157), be dropped.

(2) That the method described in last year's report [*This Journal*, 16, 563 (1933)] for the determination of milk proteins in milk chocolate be adopted as tentative.

(3) That the method described in this year's report on cacao butter for the determination of the silver number of fats be adopted as tentative (see p. 64).

(4) That the polariscopic method for the determination of sucrose and the copper-reduction method for the determination of lactose described in the report for 1932 [*This Journal*, 16, 565 (1933)] be changed from tentative to official (first action).

(5) That further work on milk proteins, cacao butter, sucrose and lactose be discontinued except in connection with the determination of milk solids.

(6) That work be renewed on the determination of cacao shell.

(7) That collaborative work be conducted on the determination of milk solids in milk chocolate.

#### COFFEE

It is recommended that the note suggested by the referee be added to the official method (*Methods of Analysis*, A.O.A.C., 1930, 151, 14) and to the tentative method for caffeine (p. 151, 15), (see p. 63).

#### GUMS IN FOODS

It is recommended that the study of methods for gums be continued.

#### FATS AND OILS

It is recommended—

(1) That the methods of analysis for cottonseed described by the referee be adopted as official (first action), (see p. 70).

Approved, with a recommendation by the Committee that these methods be included in the chapter on Oils, Fats and Waxes under the title, "Methods of Analysis of Cottonseed for Crushing Purposes."

(2) That the study of the refractometric method for the determination of oil in oleaginous seeds be continued.

(3) That collaborative study be undertaken on the determination of the hydrogen number of fats and oils in comparison with the acetyl value determination.

(4) That collaborative study be undertaken on the preparation of aldehyde-free alcohol.

#### MICROCHEMICAL METHODS

It is recommended that the referee subject to collaborative study the methods for which there appears to be need.

#### MICROBIOLOGICAL METHODS

It is recommended that studies of methods for microbiological examination of canned foods be undertaken, with special attention to the following: (a) Treatment of the container before opening; (b) proper subsampling procedures; (c) suitable culture medium for non-acid products; (d) suitable culture medium for acid products; and (e) incubation times and temperatures for cultures.

### CHANGES IN THE OFFICIAL AND TENTATIVE METHODS OF ANALYSIS MADE AT THE FORTY-NINTH ANNUAL CONVENTION, NOVEMBER 6-8, 1933<sup>1</sup>

#### I. SOILS

No additions, deletions, or other changes.

#### II. FERTILIZERS

(1) The first of the alternative methods for preparing ammonium citrate solution [p. 17, 13(1)]<sup>2</sup> was deleted (final action). This action also includes the deletion of the preceding sentence, "prepare according to either," etc.

(2) The method published last year [*This Journal*, 16, 68 (1933)] for the preparation of ammonium citrate solution was adopted as official (final action).

(3) In the official volumetric method for the determination of water-soluble phosphoric acid (p. 17, 12) the following section in the second line: "to 0.2 or 0.4 g," was changed to read "to 0.1, 0.2 or 0.4 g" (first action).

#### III. SEWAGE\*

#### IV. AGRICULTURAL LIMING MATERIALS

No additions, deletions, or other changes.

#### V. AGRICULTURAL DUST\*

#### VI. INSECTICIDES AND FUNGICIDES

(1) The electrolytic method (Method II) for the determination of lead

<sup>1</sup> Compiled by Marian E. Lapp, Associate Editor.

<sup>2</sup> Unless otherwise given all references in this report are to *Methods of Analysis*, A.O.A.C., 1930, and the methods are edited to conform to the style used in that publication.

\* Subjects for future study.

oxide and copper in Bordeaux-lead arsenate mixtures [*This Journal*, 16, 69 (1933)] was adopted as an official method (final action).

(2) The Willard-Winter method for the determination of fluorine [*Ind. Eng. Chem. Anal. Ed.*, 5, 7 (1933); *This Journal*, 16, 105 (1933)] was adopted as a tentative method.

#### VII. CAUSTIC POISONS

No additions, deletions, or other changes.

#### VIII. NAVAL STORES

No additions, deletions, or other changes.

#### IX. PAINTS

No additions, deletions, or other changes.

#### X. LEATHERS

No additions, deletions, or other changes.

#### XI. TANNING MATERIALS

No additions, deletions, or other changes.

#### XII. PLANTS

The method recommended by the associate referee for the determination of nitrate nitrogen in plant tissue [*This Journal*, 16, 474 (1933)] was adopted as a tentative method.

#### XIII. FIBERS\*

#### XIV. PAPER AND PAPER MATERIALS\*

#### XV. BAKING POWDERS AND BAKING CHEMICALS

No additions, deletions, or other changes.

#### XVI. BEVERAGES (NON-ALCOHOLIC) AND CONCENTRATES

No additions, deletions, or other changes.

#### XVII. BEERS, WINES, AND DISTILLED LIQUORS

No additions, deletions, or other changes.

#### XVIII. COFFEE AND TEA

The following note, suggested by the referee, was added to the official method for the determination of caffeine (p. 151, 14) (first action) and also to the tentative method for the same determination (p. 151, 15):

In the case of products very low in caffeine combine the caffeine residues from duplicate determinations (thus representing 20 g of original material) and determine nitrogen as directed in II, sec. 19 or 22, using half the quantity of reagents called

for in the digestion and steaming out the distillation apparatus thoroughly before distilling. Distil to small volume in the distilling flask to insure removal of all ammonia. Correct for the blank obtained, using the same reagents and apparatus and pure sucrose in place of caffeine.

### XIX. CACAO BEAN AND ITS PRODUCTS

(1) The tentative method for the determination of casein in milk chocolate (p. 157, 10) was dropped.

(2) The method published last year [*This Journal*, 16, 563 (1933)] for the determination of milk proteins in milk chocolate was adopted as a tentative method.

(3) The following method for the determination of the silver number of fats was adopted as a tentative method:

#### SILVER NUMBER

##### REAGENTS

- (a) *Alcohol*.—95% by volume.
- (b) *Potassium hydroxide soln.*—750 g of KOH per liter.
- (c) *Magnesium sulfate soln.*—150 g of  $\text{Mg} \cdot \text{SO}_4 \cdot 7\text{H}_2\text{O}$  per liter.
- (d) *Sulfuric acid soln.*—Approximately 0.5 N.
- (e) *Silver nitrate soln.*—0.2 N.
- (f) *Sodium nitrate*.—Crystals as near Cl-free as practicable to obtain 0.002% or less.
- (g) *Ferric indicator soln.*—Saturated. Use ferric potassium sulfate or ferric ammonium sulfate.
- (h) *Nitric acid*.—40%.
- (i) *Ammonium thiocyanate soln.*—0.1 N.

##### DETERMINATION

Weigh 10 g of fat into a 250 cc beaker, add 40 cc of alcohol and 5 cc of reagent (d). Saponify the mixture and evaporate to dryness on the steam bath. Take up the soap in  $\text{H}_2\text{O}$  (150 cc), warming if necessary. Cool, and make up to 250 cc.

Pipet 200 cc of the soln into a 500 cc Erlenmeyer flask. Close the flask with a stopper carrying a thermometer and having a small groove lengthwise in the side. Place the flask in a water bath maintained at about 80°. When the sample reaches about 80°, loosen the stopper and introduce 50 cc of reagent (c) from a pipet. Shake the flask with a rotary motion. Replace the stopper and thermometer and allow the flask to remain in the bath 8–10 min. longer at a temp. between 70° and 80°, shaking the flask occasionally. Remove the flask and cool under the tap with shaking to 20°–25°. Remove stopper and thermometer, stopper tightly, and shake vigorously 4 min. Allow the flask to stand in a bath at 20°–25° until a water layer separates at the bottom. Filter through a Büchner funnel, removing all liquid possible by pressing with a horn spoon. Run a blank on cacao butter in the same manner.

Neutralize 200 cc of the filtrate until colorless to phenolphthalein with reagent (d) in a 250 cc volumetric flask. Add 20 g of reagent (f) and when dissolved add 22.5 cc of reagent (e). Make to mark and shake 3 min. Allow the flask to stand a short time and filter thru a folded filter. To 200 cc of the filtrate add 6 cc of reagent (g) and 4 cc of reagent (h). Titrate with 0.1 N  $\text{NH}_4\text{CnS}$  to first color change (reddish brown).

Calculate the silver number of the fat by the following formula:

Silver number =  $(a - b) \times 2.107$ , in which

Silver number = mg. of silver used per gram of fat;

$a = 8.5 \times \text{cc of } 0.2 \text{ } N \text{ silver nitrate soln. added; and}$

$b = \text{cc of } 0.1 \text{ } N \text{ } NH_4CnS \text{ soln used in back titration.}$

$$\text{Factor } 2.107 = \frac{10.788 \text{ (mg } \times \text{ Ag per cc } 0.1 \text{ } N \text{ soln)}}{5.12 \text{ (g of fat in aliquot titrated)}}$$

(4) The tentative polariscopic method for the determination of sucrose in milk chocolate [*This Journal*, 16, 565 (1933)] was adopted as official (first action).

(5) The tentative copper-reduction method for the determination of lactose in milk chocolate [*This Journal*, 16, 566 (1933)] was adopted as official (first action).

## XX. CEREAL PRODUCTS

(1) The tentative method for the determination of starch in flour was revised as suggested by the associate referee. This method, as published in *This Journal*, 16, 504 (1933), supersedes sections 35 and 36, p. 172.

(2) The  $CHCl_3$  test for the detection of rye flour in wheat flour was adopted as a tentative method. The method follows:

To 10 g of flour in a test tube, add 20 cc of  $CHCl_3$ , stopper the tube, and shake well. Allow the tube to stand in a vertical position until the heavier particles have settled out, preferably overnight. If rye is present, the sediment in the tube will be of greenish or bluish tint. Wheat gives a yellowish sediment.

Make comparisons with wheat and rye flours of known purity and with mixtures of varying proportions, such as 5 per cent, 10 per cent, 15 per cent, etc., of rye.

Treat flours containing phosphate or leavening agents with  $CCl_4$  in a separatory funnel to remove added salts. After removing the sediment of salts from the separatory funnel collect the flour on a filter, transfer to a test tube, and treat with  $CHCl_3$ .

(3) The vacuum oven method for the determination of moisture in bread (p. 177, 48) was adopted as official for the determination of moisture in all other baked products not containing fruit (final action).

(4) The  $130^\circ C$  air-oven method for the determination of moisture in bread (p. 177, 49) was adopted as an official method for this determination in all other air-dried baked products not containing fruit (final action).

(5) The official method for the determination of crude fiber in bread [p. 178, 55; *This Journal*, 16, 72 (1933)] was adopted as official for this determination in all other baked products (first action).

(6) The title "Alimentary Pastes," p. 180, was changed to "Macaroni Products."

(7) The method for the determination of diastatic power of flour recommended by the associate referee [*This Journal*, 16, 501 (1933)], was adopted as tentative.



## XXI. COLORING MATTERS IN FOODS

No additions, deletions, or other changes.

## XXII. DAIRY PRODUCTS

(1) The tentative method for the determination of tartaric acid in cheese (p. 240, 101) was adopted as official (final action).

(2) The tentative method for the determination of citric acid in cheese (p. 241, 104) was adopted as official (final action).

## XXIII. EGGS AND EGG PRODUCTS

No additions, deletions, or other changes.

## XXIV. FISH AND OTHER MARINE PRODUCTS\*

## XXV. FLAVORING EXTRACTS

No additions, deletions, or other changes.

## XXVI. FRUITS AND FRUIT PRODUCTS

(1) The Hartmann-Hillig method for the determination of *l*-malic acid [*This Journal*, 15, 648 (1932)] was adopted as a tentative method.

(2) In line 3 of the official method for the determination of moisture in dried fruits (p. 264, 3) "12 hours" was changed to "6 hours" (first action).

(3) The tentative method for the determination of moisture in dried apples (p. 265, 4) was dropped.

(4) The following method for sampling boxed dried fruits was adopted as a tentative method:

### SAMPLING OF BOXED DRIED FRUITS

Remove cover, bottom, or one side of box, as is most convenient. Remove a block comprising 1/8 of the contents of the box taken from one corner as follows: With a sharp knife make a vertical cut midway between the *ends* of the box to the center of the top surface, this cut to extend half way to the bottom. Make another vertical cut midway between the *sides* of the box, extending half way to the bottom, and continue it until it meets the first cut. Remove all apples included in the angle formed by the two cuts. Working rapidly, break up all lumps, thoroughly mix, and take sufficient sample to fill a one-quart Mason jar, replacing the remainder in the box. Seal the jar and send to the laboratory. Sample a sufficient number of boxes taken from different parts of the pile to constitute at least the square root of the lot.

## XXVII. GRAIN AND STOCK FEEDS

(1) The Knapheide-Lamb method for the determination of iodine in mineral mixed feeds was adopted as a tentative method. The method follows:

**IODINE IN MINERAL MIXED FEEDS**  
*Knapheide-Lamb<sup>1</sup> Method—Tentative*

REAGENTS

- (a) *Ethyl alcohol*.—80%.
- (b) *Phosphoric acid*.—Sirupy, or 85%.
- (c) *Salicylic acid*.
- (d) *Reduced phosphoric acid*.—20%. Reduce impurities in the  $\text{H}_3\text{PO}_4$  according to Kendall's method [*J. Biol. Chem.*, **43**, 150 (1920)] by diluting the 85% acid with 4 volumes of  $\text{H}_2\text{O}$  and boiling for some time with aluminum strips.
- (e) *Methyl orange indicator*.
- (f) *Sodium bisulfite soln*.—20%.
- (g) *Bromine water*.
- (h) *Potassium iodide*.—C.P.
- (i) *Starch soln indicator*.
- (j) *Sodium thiosulfate soln*.—0.005 *N*. Preferably standardize by pipetting into a beaker 25 cc of a soln containing 0.1308 g of KI per liter and adding 200 cc of  $\text{H}_2\text{O}$ , 5 cc of 20%  $\text{NaHSO}_3$  soln and 2 or 3 g of NaOH. Neutralize the mixture with sirupy  $\text{H}_3\text{PO}_4$ , adding 1.0 cc in excess and proceeding further as described in the regular determination. To calculate the mg of iodine to which 1 cc of the  $\text{Na}_2\text{S}_2\text{O}_3$  soln. is equivalent, use the following formula: 
$$\frac{2.5}{\text{cc of Na}_2\text{S}_2\text{O}_3 \text{ soln}}$$
 (It is well to standardize the  $\text{Na}_2\text{S}_2\text{O}_3$  soln the day the determination is made.)

APPARATUS<sup>2</sup>

**Furnace**.—Use a sheet-iron cylinder 4 inches wide and 12 inches long, and have an opening in the center of the top large enough to accommodate a 100 cc nickel crucible. Suspend a 2½ inch circular plate in the center of the cylinder 3 inches below the top, for spreading the flame, thereby preventing the free flame from coming in contact with the crucible and providing uniform heat. Make a slot at the bottom of the cylinder 1 inch wide by 3 inches high for admitting air and the burner tubing, and near the top rim make eight ¼ inch holes to allow for the escape of the exhaust gases.

DETERMINATION

Fuse together in a 100 cc nickel crucible 20 g of NaOH and 10 g of  $\text{KNO}_3$  and cool. Place evenly on top of the fused alkali a 1 to 10 g sample (depending upon its composition and the trouble experienced from frothing in the fusion) of the mineral mixture and completely moisten with 5 cc of saturated NaOH soln and 10 cc of 80% alcohol. Place the crucible on a cold three-heat hot plate and evaporate the alcohol by the low heat. After half an hour cautiously increase the heat until the crucible has been subjected to the highest temperature of the hot plate for 1½–2 hours. (Thorough heating at this time prevents most of the trouble from effervescence of the material during the fusion.) Then place the crucible in the furnace described above or in a similar furnace.

To prevent loss give close attention to mineral mixtures containing charcoal or organic matter during the fusion because of the violent reaction between the carbon and the  $\text{KNO}_3$ . If the reaction becomes too violent lift the crucible from the furnace for a moment, and if necessary cool the bottom of the crucible in a beaker of  $\text{H}_2\text{O}$ .

<sup>1</sup> *J. Am. Chem. Soc.*, **50**, 2121 (1928).  
*This Journal*, **14**, 150 (1931).

When the mixture is in a quiet state of fusion tip the crucible on all sides in an open flame to wash down the fusion mixture. Add a few small crystals of  $\text{KNO}_3$  until no more gas is liberated by further additions, and again wash down the sides of the crucible in the flame.

Pour the melt out into the clean crucible cover to cool or turn the crucible while cooling so that the material solidifies on the sides. Place the cooled melt and the crucible in a 600 cc beaker, cover with  $\text{H}_2\text{O}$ , and heat below the boiling point for a short time. After allowing the mixture to stand overnight at room temp., rinse off the crucible and cover and remove. In order to neutralize part of the alkali and facilitate filtering, add 10 cc of sirupy  $\text{H}_3\text{PO}_4$  and place the beaker on a steam bath for 3-4 hours, stirring occasionally to break up the mass and insure complete solution of the iodine. Cool the beaker, filter off the insoluble residue into a 10 cm funnel, and wash with cold  $\text{H}_2\text{O}$  into an 800 cc beaker, adjusting the volume to 550-600 cc. (The soln should be clear and colorless.)

In order to destroy nitrites, which interfere with the titration with methyl orange, add 10 cc of 20%  $\text{NaHSO}_3$ , bring the soln just to the boiling point, and cool. Run approximately 30 cc of 85%  $\text{H}_3\text{PO}_4$  in from a buret, add a few drops of methyl orange soln, continue the addition of  $\text{H}_3\text{PO}_4$  to the neutral color of the methyl orange, and finally add 1.5 cc of  $\text{H}_3\text{PO}_4$  in excess. (The total quantity of  $\text{H}_3\text{PO}_4$  required is generally not over 35 cc, except when the presence of considerable carbon in the sample has necessitated the use of more  $\text{KNO}_3$ , which is thus mainly reduced to carbonate.) Use care not to run appreciably over the end-point, as excess acid gives low results. However, the addition of the acid must be fairly rapid, as the color of the methyl orange has a tendency to fade, due to incomplete destruction of the nitrites.

After neutralization, add a small lump of anthracite coal (0.5 cm in diameter) and boil the soln for at least 20 minutes, the volume being reduced to about 400 to 500 cc. (This boiling is essential to remove all traces of sulfurous acid.) Again cool the soln and add bromine water until a distinct and permanent yellow color is produced. Boil the soln until colorless by reflected light and then for exactly 5 minutes longer. Add a few crystals of salicylic acid to assure the removal of the last traces of Br, cool the soln, and add 5 cc of 20% reduced  $\text{H}_3\text{PO}_4$  and 0.5-1.0 g of C.P. KI. Titrate the soln in the usual manner with 0.005 N  $\text{Na}_2\text{S}_2\text{O}_3$ , adding starch soln when the brown color of the liberated Br is nearly gone. (The volume of the soln at the final titration should be 400 to 500 cc.)

(2) The official method for the determination of moisture (p. 277, 2) was changed by substituting in the first line the words "at the temp. of 95°-100°" for the phrase "at the temp. of boiling  $\text{H}_2\text{O}$ " (first action).

(3) Section 2, p. 277, was also changed by omitting the provision for drying in a current of H by deleting the following clause: "or dry in a current of H at the same temp. but at atmospheric pressure" (first action).

(4) In the same method (p. 277, 2) and also in the method for the determination of moisture by the electric air-oven method (p. 278, 7) the use of covered aluminum dishes at least 50 mm. in diameter and not exceeding 40 mm. deep was specified (first action).

(5) The following method for the determination of vitamin D was adopted as a tentative method:

## VITAMIN D ASSAY BY PREVENTIVE BIOLOGICAL TEST

(Applicable to fish and fish liver oils and their extracts, and to materials used for supplementing the vitamin D content of feeds. Not applicable to irradiated ergosterol products or to irradiated yeast unless recommended for poultry.)

## BASAL RACHITIC RATION

	<i>per cent</i>
Ground yellow corn.....	59
Pure wheat flour middlings.....	25
Crude domestic acid precipitated casein.....	12
Calcium carbonate (precipitated).....	1
Calcium phosphate (precipitated).....	1
Iodized salt (.02% potassium iodide).....	1
Non-irradiated yeast (7% minimum nitrogen).....	1

## PROCEDURE

Place groups of ten or more one-day-old white leghorn chickens in screen-bottomed biological cages or battery brooder out of direct sunlight. (Red electric light bulbs are satisfactory as a source of heat for the cages.) Reserve one group for negative control purposes, and one or more additional groups for each material to be assayed. Keep distilled water before the chicks at all times.

Prepare sufficient basal rachitic ration for the entire feeding period (80 pounds per 100 birds is ample). Prepare the supplemented rations at 8-12 day periods. Supplement the basal rachitic ration with corn oil in a quantity equal to the maximum addition of the oil to be assayed. (This is the ration to be fed to the negative control group.) Supplement the basal ration with different levels of the material to be assayed. Add corn oil to bring the percentage of oil up to that added to the negative control ration. (These are the rations to be fed to the other groups.)

On the second day give the groups two 15-minute feedings of their respective rations. Beginning the third day feed the rations *ad libitum* for 28 days.

Kill the birds, remove the left tibia of each bird, and clean of adhering tissue. (To facilitate removal of adhering tissue the bones may be placed in boiling water for not more than 2 minutes.) Number the bones and place in 95 per cent ethyl alcohol. Crush, wrap individually in filter paper, and extract the bones for 20 hours with hot 95 per cent ethyl alcohol, followed by 20 hours with ethyl ether. (Other solvents may be used for this fat extraction.) Dry in a moisture oven, and store in a desiccator. Determine the percentage of ash of the moisture and fat-free bones by igniting in a muffle furnace at approximately 850° for one hour. Compile group ash averages.

(6) The Alkaline Titration Method—Tentative (p. 287, 38) was deleted.

(7) The following phrase in the last line of the Prussian Blue Method—Tentative (p. 287, 39): "from a standard soln containing 1 mg of KCN diluted to 25 cc," was changed to read, "from the vacuum evaporation of a standard soln containing 1 mg of KCN diluted to 25 cc," and the following sentence was added: "This soln, containing 1 mg of KCN = 0.415 mg of HCN."

**XXVIII. MEAT AND MEAT PRODUCTS**

The tentative method for the determination of salt [*This Journal*, 16, 75 (1933)] was adopted as official (first action).

**XXIX. METALS IN FOODS**

(1) The tentative bromate method for the determination of arsenic on fresh fruit [*This Journal*, 16, 75 (1933)] was revised by substituting hydrazine sulfate for ferrous sulfate (f) for reduction purposes.

(2) The use of the bromate method was restricted to the determination of arsenic in fruits and vegetables in which a sample containing at least 0.005 grain or 0.3 mg of  $\text{As}_2\text{O}_3$  can be digested.

**XXX. NUTS AND NUT PRODUCTS\*****XXXI. OILS, FATS AND WAXES**

The methods of analysis for cottonseed for crushing purposes compiled and issued by the U. S. Department of Agriculture<sup>1</sup> were adopted as official (first action) and are to be published in the chapter on Oils, Fats and Waxes under an appropriate title.

**XXXII. PRESERVATIVES AND ARTIFICIAL SWEETENERS**

(1) The Monier-Williams method (p. 344, 34) for the determination of total sulfurous acid, including the alterations published last year [*This Journal*, 16, 77 (1933)], was made an official method (first action).

(2) The official methods for the determination of sulfurous acid (pp. 343, 344, 31, 32) were dropped (first action).

(3) Line 6 of the qualitative test for sulfurous acid (p. 343, 30) was changed to provide verification of positive results by the Monier-Williams method (first action).

(4) The directions of the official quantitative method for the determination of boric acid (p. 340, 16), were changed to provide for the use of 1-2 grams of mannitol instead of 10 grams for the titration (final action).

**XXXIII. SPICES AND OTHER CONDIMENTS**

(1) The following methods for the determination of volatile oil, specific gravity, optical rotation, refractive index, eugenol, and acid and ester numbers of separated oil, were adopted as tentative:

1

**VOLATILE OIL IN SPICES**

Transfer a weighed quantity of whole or ground material to a 500-2000 cc round-bottomed, short-necked flask in amount sufficient to yield, if possible, 2 cc or more of volatile oil. Add to the flask 3-6 times as much  $\text{H}_2\text{O}$  as material and mix uniformly. Set up apparatus as indicated in Fig. 1, using the appropriate volatile oil trap illustrated in Fig. 2. With an oil bath (hydrogenated cottonseed oil is satisfactory) as the source of heat, boil the contents of the flask slowly 4-8 hours, or until

<sup>1</sup> U. S. Dept. Agr. Agricultural Economics, S R A. 133, August, 1932.

all the volatile oil has been distilled, taking care to avoid the escape of vapors around the condenser. (With spices, for example nutmeg, containing volatile oils lighter than  $H_2O$  and also fixed oils heavier than  $H_2O$  discontinue the distillation when the fraction of oil obtained during a 1 hour period is heavier than  $H_2O$ .)

In case of unsatisfactory separation of the volatile oil, draw off the contents of the trap into a small separatory funnel. After separation return the  $H_2O$  to the trap

#### APPARATUS FOR THE DETERMINATION OF VOLATILE OIL

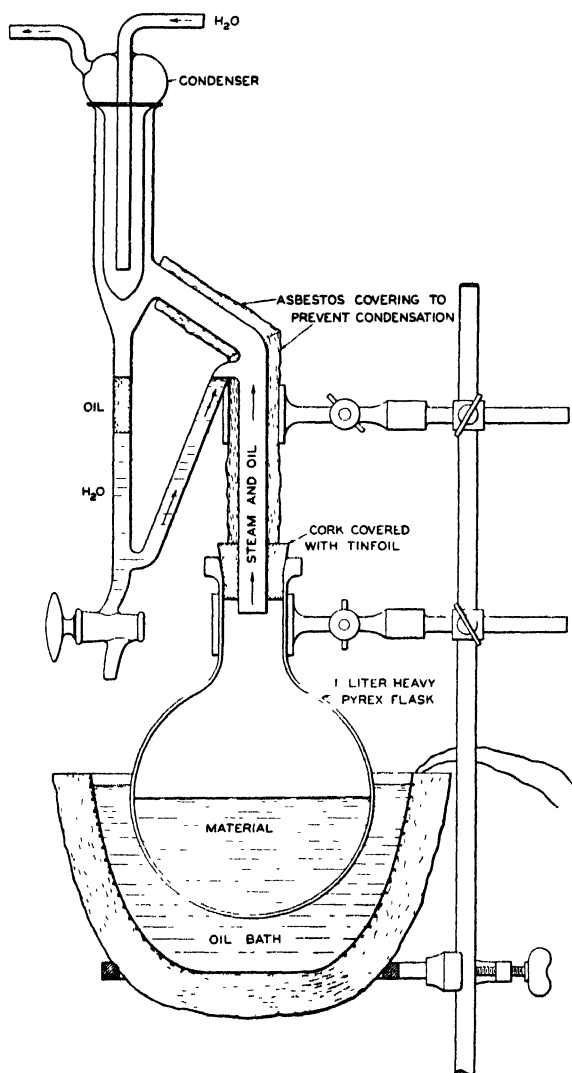


FIG. 1



2

**SPECIFIC GRAVITY**

Determine specific gravity at 25/25° as directed on p. 136, 24, using a 1 cc Sprengel tube.

3

**OPTICAL ROTATION**

Polarize in a micropolarizing tube 50 mm long and approximately 2 mm bore. (The tube may be readily filled by the aid of a glass tube drawn out to a diameter smaller than the bore of the tube.)

4

**REFRACTIVE INDEX**

Proceed as directed on p. 315, 7 and 8.

5

**ACID NUMBER**

Add 30 cc of neutral alcohol to approximately 2 g of the volatile oil, accurately weighed, in a 200 cc Erlenmeyer flask. Titrate with 0.1 N KOH, using 1-2 drops of 1% phenolphthalein as an indicator. Calculate the acid number by means of the

following formula: 
$$\frac{\text{cc } 0.1 \text{ N KOH} \times 5.61}{\text{Wt. of volatile oil}}$$

6

**ESTER NUMBER**

To the contents of the flask after determination 5, add exactly 20 cc of 0.5 N KOH. Heat the flask on a water bath approximately 2 hours, using an air condenser 70-80 cm long and 5-8 mm in diameter. Determine the cc (a) of 0.5 N KOH used in the saponification by titrating the excess with 0.5 N H<sub>2</sub>SO<sub>4</sub>, using 1-2 drops of phenolphthalein as an indicator. Calculate the ester number by means of the following formula:

$$\frac{(a) \times 28.06}{\text{Wt. of volatile oil}}$$

7

**EUGENOL**

Measure 2 cc of volatile oil (transfer pipet) into a Babcock milk bottle [p. 217, 18(a)]. Add 20 cc of 3% soln of KOH, shake the mixture 5 min., heat for 10 min. in a boiling water bath, remove, and cool to room temp. When the liquids have separated completely, add sufficient KOH soln to bring the residual oil within the graduated portion of the neck and note the volume. The percentage by volume of eugenol is calculated from the difference of volume of the sample used and the residual oil.

(2) The changes in the official method for the determination of glycerol in vinegar (pp. 358, 360, 62, 63), published in *This Journal*, 15, 536 (1932), were adopted as official (first action).

(3) The methods for the determination of total solids, acidity, nitrogen and P<sub>2</sub>O<sub>5</sub> in salad dressings, adopted as official, first action, and published last year [*This Journal*, 16, 77, 78 (1933)], were adopted as official (final action).

**XXXIV. SUGARS AND SUGAR PRODUCTS**

(1) The sentence, "To facilitate the filtration a hot water funnel, suction or a filter-aid may be employed," in the tentative method for the preparation of sample under maple products in section 103(a), par. 2, p. 391, was deleted.

(2) The method referred to above was adopted as an official method (first action).



(3) The directions for preparing the reagent used in the determination of the Winton lead number (115, p. 392) were changed as published last year [*This Journal*, 16, 80 (1933)] and adopted as official (final action).

(4) The directions for preparing the reagent used in the determination of the Canadian lead number (Fowler modification, 118, p. 393), were changed as published last year [*This Journal*, 16, 80 (1933)] and adopted as official (final action).

(5) The directions for determining conductivity value (official, first action), p. 393, 120, as revised last year [*This Journal*, 16, 80 (1933)] and adopted as official (first action), were adopted as official (final action).

(6) The change in the official method for the determination of moisture in maple sirup (p. 391, 104), published last year and adopted as official, first action [*This Journal*, 16, 79 (1933)], was adopted as official (final action).

(7) The change in the method for the determination of sucrose in the absence of raffinose (p. 392, 107), published last year and adopted as official, first action [*This Journal*, 16, 79 (1933)], was adopted as official, (final action).

(8) The changes [Nos. (1), (2), (3) and (4)] in the official methods for preparation and use of clarifying reagents [p. 368, 18(a), (b), (d) and (e)], adopted as official, first action, last year [*This Journal*, 16, 78-9 (1933)], were adopted as official (final action).

(9) The amendment to the official refractometric method for the determination of solids (p. 365, 7), adopted as official, first action, last year [*This Journal*, 16, 81 (1933)], was adopted as official (final action).

(10) Sections 32 and 33, p. 377 (tentative) were deleted.

(11) Section 44, p. 381 (official) was deleted (first action).

(12) The official Soxhlet-Wein method, 55 and 56, p. 384, was deleted (first action).

#### XXXV. VEGETABLES AND VEGETABLE PRODUCTS

No additions, deletions, or other changes.

#### XXXVI. VITAMINS\*

#### XXXVII. WATERS, BRINE, AND SALT

No additions, deletions, or other changes.

#### XXXVIII. RADIOACTIVITY OF FOODS AND DRUGS

No additions, deletions, or other changes.

#### XXXIX. DRUGS

(1) The following method for the determination of calcium gluconate was adopted as a tentative method:

## CALCIUM GLUCONATE

(Applicable to preparations whose aqueous solns are neutral and which do not contain salts of other optically active hydroxy acids.)

## REAGENTS

- (a) *Absolute ether.*
- (b) *Uranyl acetate.*—Finely pulverized.
- (c) *Uranyl acetate soln.*—Shake 10 g of uranium acetate with 95 cc of  $H_2O$  until the soln is saturated and filter.
- (d) *Alumina cream.*—Prepare as directed in 18(b), p. 368.

## DETERMINATION

Weigh two 0.5 g portions of calcium gluconate or two 1 g portions of the powdered material in the case of tablets containing 50% or less of the salt. If chocolate or a fatty base is present, wash the samples several times on a hardened filter with absolute ether and warm the residue until the ether is driven off. Transfer each portion to a separate 25 cc volumetric flask, add 15 cc of  $H_2O$ , and warm until the calcium salt is dissolved (there will be an undissolved residue in the case of samples containing cocoa). Cool to room temp. To one flask (No. 1) add 3.5 g of reagent (b), stopper, and place the mixture in a shaking machine for 1 hour (if agitation is not sufficiently vigorous, more than 1 hour's shaking may be required). Allow the other flask (No. 2) to stand. If the sample contains chocolate, add a little alumina cream to each flask and cool to  $20^\circ$ . Make up the contents of each flask to volume with reagent (c) in the case of flask No. 1 and with  $H_2O$  in the case of flask No. 2. Filter, and polarize each soln in a 200 mm tube, using a 50 mm tube containing a 1.8% soln of  $K_2Cr_2O_7$  as a light filter. If the soln is too dark to read in the 200 mm tube, make the reading in a 100 mm tube and multiply the result by 2. If  $A$  equals the rotation in  $^\circ V.$  of soln No. 2 and  $B$  the rotation of soln No. 1, with 1 g samples the percentage of  $Ca(C_6H_{11}O_7)_2 = 4.34 (B - A)$ , and with 0.5 g samples the percentage of  $Ca(C_6H_{11}O_7)_2 = 8.52 (B - A)$ .

(2) The following tests for purity of mercurochrome were adopted as tentative:

## TESTS FOR PURITY OF MERCUROCHROME

- (a) Acidify a portion of the mercurochrome soln with 10%  $H_2SO_4$  and filter off the precipitate. The filtrate is only slightly yellow colored.
- (b) Pass  $H_2S$  into a portion of the filtrate. No precipitate or coloring occurs.
- (c) Add a few cc of 10%  $HNO_3$  to another portion of the filtrate and add  $AgNO_3$  T. S. No precipitate forms.

(3) The following method for the determination of total solids in mercurochrome soln was adopted as tentative:

## TOTAL SOLIDS IN MERCUROCHROME SOLUTION

Pipet 10 cc of the mercurochrome soln into a tared, extra-wide-form weighing bottle and evaporate to dryness on a steam bath. Allow to dry overnight in a  $H_2SO_4$  desiccator in the open bottle. Remove the cover from the desiccator, quickly insert the ground-glass stopper into the weighing bottle, weigh, and report as grams per 100 cc of soln.

(4) The following method for the determination of mercury in mercurochrome was adopted as tentative:

## MERCURY IN MERCUROCHROME

## REAGENTS

- (a) *Potassium permanganate*.—Use the finely pulverized salt.
- (b) *Oxalic acid*.—Use the finely pulverized acid.
- (c) *Alcohol*.—95%.
- (d) *Carbon tetrachloride or carbon disulfide*.
- (e) *Ether*.—U.S.P.

## DETERMINATION

Pipet 10 cc of an approximately 2% soln of the mercurochrome into a 500 cc tall-form beaker and evaporate to dryness on the steam bath (or weigh accurately about 0.2 g of the powder). Dissolve the residue in 4 cc of  $H_2O$  and add slowly, with constant mixing, 10 cc of  $H_2SO_4$ . Incline the beaker and add cautiously small portions of reagent (a), mixing after each addition, until considerable excess has been added, as indicated by the deep purple color of the mixture. Allow to stand 30 min., occasionally mixing, at the end of which time the mixture should still retain its purple color. Add 100 cc of  $H_2O$  and mix thoroly. Then add small portions of reagent (b), mixing after each addition, until the soln is clear. Filter through a small filter into a 400 cc beaker, wash the original beaker, filter until the filtrate measures approximately 200 cc, and pass  $H_2S$  through the soln for 20 min. Warm on a steam bath until the precipitate of  $HgS$  settles quickly after stirring, and again pass  $H_2S$  thru the warm soln for 5 min. Filter the soln immediately into a weighed Gooch crucible, and wash the precipitate on the filter well with  $H_2O$ , three times with the alcohol, and then with four or five portions of reagent (d) to remove any sulfur that may be present, allowing the liquid to run through the crucible without suction, and finally wash with ether. Dry the precipitate to constant weight at  $100^\circ$ , and weigh as  $HgS$ . Test the dried precipitate qualitatively for Hg and other heavy metals. (If any difficulty is experienced by the slow filtration during the washing with  $H_2O$ , allow the precipitate to drain and wash once with alcohol; then continue as directed.)

Weight of  $HgS \times 0.8622$  = the equivalent weight of Hg.

Report the Hg as grams per 100 cc of soln and as percentage of Hg in the solids, as calculated from the total solids and the total Hg found.

(5) The following methods for the identification of papaverine and procaine were adopted as tentative.

## PAPAVERINE AND PROCAINE

## REAGENTS

- (a) *Zinc chloride soln*.—Dissolve 5 g of  $ZnCl_2$  in 100 cc of  $H_2O$ .
- (b) *Platinic chloride soln*.—Dissolve 5 g of  $H_2PtCl_6$  in 100 cc of  $H_2O$ .

## PREPARATION OF SAMPLE

*Controls*.—Dissolve 1 mg of the pure alkaloids salt in two drops of  $H_2O$  to make approximately 1:100 soln.

## IDENTIFICATION

To a drop of the alkaloidal soln on a clean glass slide, add a drop of reagent by means of a clean glass rod; and, without stirring or covering, examine under the microscope, using low power. A magnification of 100–180 is suitable. Note the kind of crystals formed, and compare their characteristics with the description given and then with a control.

*Characteristic Microchemical Tests for Alkaloids*

<i>Alkaloid</i>	<i>Reagent</i>	<i>Description of Crystals</i>
Papaverine	Zinc chloride	Thin rectangular plates in excess hydrochloric acid.
Procaine hydrochloride	Platinic chloride	Spherical crystals of radiating branches.
	Gold chloride and HCl	Irregular radiating branches.

(6) The following microchemical methods for the determination of antipyrine, methenamine and triethanolamine were adopted as tentative:

**ANTIPYRINE, METHENAMINE AND TRIETHANOLAMINE****REAGENTS**

(a) *Potassium ferrocyanide*.—Dissolve 5 g of  $K_4Fe(CN)_6 \cdot 3 H_2O$  in 100 cc of  $H_2O$ .

(b) *Mercuric chloride*.—Dissolve 5 g of  $HgCl_2$  in 100 cc of  $H_2O$ .

(c) *Silicotungstic acid soln*.—Dissolve 5 g of  $4 H_2O \cdot SiO_2 \cdot 12 WO_3 \cdot 5 H_2O$  in 100 cc of approximately 6 *N*  $H_2SO_4$ .

(d) *Kraut's reagent*.—Dissolve 8 g of  $Bi(NO_3)_3 \cdot 5 H_2O$  in 20 cc of  $HNO_3$ , sp. gr. 1.18. Dissolve 27.2 g of KI in 50 cc of  $H_2O$ . Mix the solns and dilute to 100 cc.

**PREPARATION OF SAMPLE**

Separate the compound for microchemical testing in pure form by the use of suitable solvents. Prepare a soln of 1:100 to 1:1000 concentration with the aid of acid, alkali or  $H_2O$  as specified for the individual synthetics.

*Controls*.—For comparison, prepare a soln of the pure synthetic in the concentration specified for each.

**IDENTIFICATION**

To a drop of a soln of the compound on a clear glass slide, add a drop of the specified reagent, and without stirring or covering examine under the microscope. A magnification of 100–150 is suitable. Note the characteristics of the crystals formed and compare with control and description.

<i>Synthetic</i>	<i>Solution</i>	<i>Concentration</i>	<i>Reagent</i>	<i>Description of crystals</i>
Antipyrine	Dissolve in water	1:100	Potassium ferrocyanide	Acicular and prismatic crystals form after adding a drop of 1% HCl.
Methenamine	"	1:500	Silicotungstic acid	Thin transparent rectangular crystals
Triethanolamine	"	1:100	Kraut's reagent	Oily globules changing to large red hexagonal plates and prismatic crystals

(7) The method proposed last year for the determination of ether [*This Journal*, 16, 357 (1933)] was adopted as tentative, with the addition of

the following explanatory note, "Not applicable in the presence of essential oils."

(8) The method for preparing standard bromide-bromate soln [p. 439, 5(a)] was amended to read: "Dissolve 14 g of  $\text{KBrO}_3$  and 55 g of  $\text{KBr}$  in  $\text{H}_2\text{O}$ . Dilute to 1 liter and standardize the soln either against recrystallized and dried acetanilid according to 4(b),\* beginning with the following sentence in the second paragraph: Add 10 cc of  $\text{H}_2\text{SO}_4$  (1+9), or, transfer 10 cc of the bromide-bromate soln to a glass-stoppered flask and add 25 cc of  $\text{H}_2\text{O}$ , 5 cc of  $\text{KI}$  soln and 5 cc of  $\text{HCl}$ . Shake thoroughly and titrate the liberated  $\text{I}$  with 0.1  $N$   $\text{Na}_2\text{S}_2\text{O}_3$  soln, using starch soln as indicator [p. 35, 3(e)].

(9) The method for preparing standard bromide-bromate soln [p. 446, 25(c)] was amended by changing "50 g" in the second line of the paragraph to "12 g\*."

\* (NOTE.—In both cases a slight excess of  $\text{NaBr}$  has been provided, because the U.S.P. salt need contain only 93.6% of  $\text{KBr}$ , that is 98.5% of  $\text{KBr}$  after allowance for 5% of  $\text{H}_2\text{O}$ .)

(10) The last sentence in the first paragraph of 7(b), p. 441, was changed to the following: "Each cc of 0.5  $N$  bromide-bromate soln equals 0.01126 g of acetanilid," and the following paragraph was added: "Acetanilid may also be determined by adding an excess of the standard bromide-bromate soln to the soln of anilin sulfate obtained as directed in (b) and titrating back the excess with 0.1  $N$   $\text{Na}_2\text{S}_2\text{O}_3$  after the addition of 5 cc of  $\text{KI}$  soln and starch soln as indicator [p. 35, 3(e)]. Each cc of 0.1  $N$  bromide-bromate soln = 0.002252 g of acetanilid."

(11) Paragraph 19(b), p. 445, was amended by adding after the expression "0.1  $N$  bromide-bromate soln" the expression, "25(c)."

(12) The following method for the determination of tetrachlorethylene was adopted as a tentative method:

#### TETRACHLORETHYLENE

##### REAGENTS

(a) *Xylene.*

(b) *Metallic sodium.*—For each determination heat on a hot plate 2 g of metallic sodium in xylene in a small Erlenmeyer flask fitted with a glass stopper, until the sodium is melted. Shake to remove excess vapor, stopper, wrap in a towel, and shake vigorously until the sodium is finely divided. Cool. Remove the xylene and replace with 5 cc. of fresh xylene.

(c) *Amyl alcohol.*

(d) *Nitric acid.*

(e) *Silver nitrate soln.*—0.1  $N$ .

(f) *Ammonium or potassium thiocyanate soln.*—0.05  $N$ . Adjust by titrating against 0.1  $N$   $\text{AgNO}_3$  soln.

(g) *Ferric ammonium sulfate.*—Dissolve 8 g of  $\text{FeNH}_4(\text{SO}_4)_2 \cdot 12 \text{H}_2\text{O}$  in sufficient  $\text{H}_2\text{O}$  to make 100 cc.

## PREPARATION OF SAMPLE

Transfer approximately 10 cc of xylene to a 125 cc Erlenmeyer flask, close with a cork stopper, and weigh carefully. Remove from the balance pan, open, and from a split cc pipet with the tip just above the surface of the xylene, add about 0.16 g (equivalent to approximately 0.10 cc of  $C_2Cl_4$ ) of the sample. (Do not add more than 0.20 g.) Avoid having the flask open longer than necessary, 15 seconds being a convenient time. Stopper securely and weigh again. Determine the weight of sample by difference.

## DETERMINATION

Add to the sample 2 g of reagent (b). Connect the flask with a reflux condenser, using a cork stopper, and heat on a hot plate to boiling. Then add by means of the condenser about 1 cc of amyl alcohol. Reflux gently for 2 hours, and add at intervals 1 cc portions of amyl alcohol until they total 5 cc. Disconnect the flask. When cool destroy the excess sodium with the cautious addition of 20 cc of  $H_2O$ . After all action has subsided, acidify with  $HNO_3$  and transfer to a separator. Shake the xylene layer with three 10 cc portions of  $H_2O$ . Combine the acid aqueous solns in a 200 cc volumetric flask. Pipet 50 cc of reagent (e) into the flask and make up to 200 cc. Shake thoroly and pour thru a dry filter, discarding the first 20 cc. To a 100 cc aliquot add 3 cc of reagent (g) as indicator. Titrate the excess of reagent (e), using reagent (f) as indicator. Make a blank test for chloride and apply whatever correction may be necessary. 1 cc of 0.1 N  $AgNO_3 = 0.004146$  g tetrachlorethylene ( $C_2Cl_4$ ).

NOTE.—The chloride may be determined gravimetrically. 1 g of  $AgCl = 0.28926$  g of  $C_2Cl_4$ .

(13) The following directions for preparing samples for the analysis of tablets or pills containing strychnine, to be substituted for the first two sentences of 106, p. 472, were adopted as official (first action):

Count and weigh sufficient tablets (or pills) to represent 1 grain of the alkaloidal salt and transfer to a small beaker. If the color on coated tablets interferes with the indicator in titration, wash without removing strychnine, add 10 cc of 5%  $HCl$ , disintegrate the tablets with a stirring rod, warm on the steam bath about 10 min., cool, and transfer to a separator with not more than 10 cc of  $H_2O$ . To remove all the strychnine, add to the beaker 2 cc. of  $NH_4OH$  and 25 cc of  $CHCl_3$ , rinse, and add to separator. Then rinse the beaker with the portions of  $CHCl_3$  to be used for each extraction.

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The motion was made, seconded and adopted that referees and associate referees be appointed without delay to take care of the chapters in *Methods of Analysis* for which no referees have been appointed.

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No report was given by the Committee on Standard Scale for Immersion Refractometer.

## REPORT OF COMMITTEE TO COLLABORATE WITH AMERICAN PUBLIC HEALTH ASSOCIATION ON METHODS OF MILK ANALYSIS

A year ago your Committee reported that a revision of Part II of Standard Methods of Milk Analysis of the American Public Health Association had been prepared and submitted to the secretary on methods of that association. The revision submitted followed exactly the descriptions of methods contained in *Methods of Analysis* of our Association for the analysis of milk, cream and ice cream. Methods for the determination of active or available chlorine were included at the request of the American Public Health Association and with the permission of authorities from which those methods were quoted. The Committee now reports favorable action by the American Public Health Association on the revision submitted.

During the year your Committee has had repeated inquiries concerning modified Babcock methods for the determination of fat in ice cream. To all such questions the reply has been made that our Association has adopted only the Roese-Gottlieb method and that we are not in a position to adopt or to recommend any rapid, modified Babcock method at this time. The work of the Referee on Dairy Products, during the past year, has been for the purpose of meeting this need if it can be met.

E. M. BAILEY  
F. C. Blanck  
G. G. FRARY

Approved.

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## REPORT OF REPRESENTATIVES ON BOARD OF GOVERNORS OF THE CROP PROTECTION INSTITUTE

The following is a brief summary of the projects prosecuted during the past year under the auspices of the Crop Protection Institute:

1. A search was made for new and better copper compounds adapted for control of plant diseases and intended to eliminate the plant injury often caused by present compounds.
2. A study was made of copper salts in relation to plant nutrition and plant stimulation. This work is yielding results that appear to shed new light upon the relation of copper to plant growth.
3. In the investigation of oil sprays for application to plants, two materials that were developed in the course of this work are on the market and additional combinations and materials are in process of development.
4. Investigations are being conducted on plant introduction and improvement, with promise.

5. Colloidal or flotation sulfur developed in the course of a project carried on with the cooperation of the agricultural experiment stations of Illinois and New Jersey is now in extensive use by fruit growers.

6. Extensive data have been accumulated as to the best methods of extracting pyrethrum flowers for the manufacture of sprays intended for application to plants and the best methods of impregnating inert dusts with the active principle of pyrethrum flowers.

7. There has been developed a practical method of using industrial adhesive tape in such a way as to reduce losses from crown gall.

8. A study of the relation of oil sprays to the control of fruit moth has been brought to a close.

9. At the Washington Agricultural Experiment Station a part-time study was made of oil sprays for the control of the codling moth.

10. A preliminary study of some new contact insecticides has developed some promising materials which are in process of preparation for commercial use.

11. In cooperation with the New Jersey Agricultural Experiment Station a part time project was carried on to study iodine salts as fungicides, and aided by the Iodine Educational Bureau, Inc., it has been concluded.

12. Work has been started on a thorough search of the possibilities of certain groups of chemicals as new contact insecticides.

13. A study of the use of carbon dioxide in connection with fumigation and in connection with the application of spray materials is under way. Extensive data have been secured as to practical utilization of carbonic dioxide in connection with toxic gases that would be dangerous otherwise.

14. In cooperation with the New Jersey Agricultural Experiment Station new fungicides compatible with oil sprays have been developed, one or more of which offers definite promise.

15. Several new materials of apparently marked significance have been discovered in a search of an extensive group of organic compounds which have not hitherto been explored. This work on new contact insecticides combined with new fungicides is being carried on at the New Hampshire and the Delaware experiment stations.

16. A preliminary study was made of the development of new insecticides from certain chlorinated compounds. So far one new compound has been devised and it is giving excellent and important results.

H. J. PATTERSON  
W. H. MACINTIRE

Approved.



## REPORT OF SECRETARY-TREASURER

Before I present this report I should like to make an observation. As I sat here and listened to the reports of the committees on the work of referees my mind ran back over past years and I could not help but think how smoothly they are now presented and accepted. The members of the Association present at each meeting have lost something, perhaps, in their inability to listen to reports of the referees but the efficiency in the way these reports are now handled I believe is such that what we have lost is more than made up for in the splendid way the work of the Association is going forward. Dr. Bailey and members of these several committees certainly deserve thanks for the many hours devoted to this work. It is the culmination of the splendid work done throughout the year by the referees and associate referees.

One resignation in the list of referees and associates was received during the year, that of Llewelyn Jones, Associate Referee on Starch in Flour. V. E. Munsey, U. S. Food and Drug Administration, was appointed to fill the vacancy. The Referee on Sugars and Sugar Products, J. A. Ambler, and the Associate Referee on Ash in Flour, Alimentary Paste, and Baked Products; Chloride in Flour and Baked Products; and Color in Flour, D. A. Coleman, submitted their resignations when they submitted their reports for this year. These two vacancies will be filled by the regular procedure in the appointment of referees.

In response to a request from C. S. Ladd, Office of Food Commissioner and Chemist, Bismarck, N.D., that the moisture method on salt be modified according to directions submitted, it is considered advisable to reappoint a referee on waters, brine and salt. At the request of G. S. Jamieson, an Associate Referee on Oleaginous Seeds was appointed last year to serve under the Referee on Fats and Oils.

Death took a heavy toll of our members last year, and it was hoped that no loss would occur this year, but we have received word of the passing of Ernest Smith, Chief of the St. Louis Station, of the Food and Drug Administration, and early in the year Sam Wiley of Baltimore, an associate member of the Association, died. The Committee on Necrology will prepare a more extended notice.

Many of our members are availing themselves of the discount on books which the Association is able to obtain from book dealers. In this time of stress and poverty perhaps the Association could render further service if more of its members desire to take advantage of it and obtain the discount of from 10 to 25 per cent allowed the Association.

The division of our meeting into sections is working satisfactorily. If there are any comments I should be glad to have them either now or during the year. In the sectional meetings there seems to be keener interest, and better and freer discussion than is possible in the general meetings

results. The general meetings might lose something by this, but again I think the Association is gaining by this sectional activity.

Next year will be the 50th anniversary of the organization of this Association. The Executive Committee discussed the program for next year in relation to what we might do in celebration of that occasion. I shall be glad at any time within the next few months to receive suggestions from any member as to what we might do to make this 50th anniversary a great affair. Two suggestions have already been submitted: (1) to issue a supplement of *The Journal*; (2) to issue a special program. Probably the two can be combined, and a souvenir issue prepared which will give the history and accomplishments of the Association.

Those of you who attended the dinner last night will agree with me that it was an enjoyable affair, but I am always at a loss to know what to do about this function. The Association has no social activities, that is it ordinarily does not have, and it is rather difficult to organize this dinner, which I have been requested to look after by Dr. MacIntire and some others. I am always very glad to place the accommodations of the Cosmos Club at your disposal, but I shall cite an example of the uncertainty of this job. I was supposed to have all subscriptions for the Club by Monday evening, and at 4 o'clock I had 17 subscribers. I kept the list open and at the Club that evening I had 32. I had to make a guarantee to the Club, so I told the manager I'd guarantee 30 and to lay covers for 35. Tuesday morning I had 37 subscribers. At 12, noon, the number was increased to 43. When we got to the Club last night, the last person to come in did so after everybody was assembled and he was the 49th. We are glad to have you come, but it is very difficult for the Cosmos Club to handle the matter because the waiters have to be engaged at 10 in the morning. There is plenty of food there but no way to serve it without waiters. I am reporting this particularly in reply to some of Dr. MacIntire's facetious remarks last night.

I am able to report to you that during this past year of stress we had practically all our money in places of security. There are still such banks. There was a small loss. The Commercial National Bank, which carried one of our accounts, had \$240.82. That bank has only paid back 20 per cent so far, which for us amounted to \$48.16. The Federal American Bank also carried a small account, \$73.94, on which \$36.93 has been paid. Last year this matter of handling our funds was discussed. I asked the Executive Committee to authorize the treasurer to invest our funds, accumulated from the sale of *Methods of Analysis*. Authority was granted, and certain funds were drawn from the bank and invested in Government bonds and in the building and loan association where we carry our savings.

I shall pass on to the report of the treasurer, which is part of the secretary's report. The Association is now in a position, where at the time of

the next issue of the book of methods, we shall be able to pay cash for the 5,000 copies when printed and thereby take the discount and also pay any other bills which we may have presented to us and take the discount. For many years the Association was not in such a position. Prior to the last printing of the book of methods the printing company had to finance the issue, we paying only for those books which we drew. The treasury is in a very healthy condition even in these times of depression. Later you will hear the report of the Auditing Committee. The chairman of that Committee has suggested to me the advisability of expanding our system of accounting and I propose during the year to revise it. This should make the job of auditing less laborious to the Committee.

The detailed financial statement follows.

#### RECEIPTS

<i>Methods of Analysis</i>		
Number	Price Each	
11	\$5.50	\$60.50
279	5.00	1,395.00
140	4.40	616.00
236	4.00	944.00
18	3.92	70.56
		2.21
Total.....		\$3,088.27

#### *Journal*

Number	Price each	
48	\$5.50	\$264.00
282	5.00	1,410.00
33	4.50	148.50
88	4.40	387.20
256	4.00	1,024.00
8	1.50	12.00
9	1.25	11.25
1	1.10	1.10
1	1.00	1.00
1	2.77	2.77
		\$3,261.82
Minus charge for exchange.....		\$11.15
Minus tax on checks.....		1.20
Minus returned checks.....		44.00
Minus redeposited checks.....		27.00
		83.35
		\$3,178.47

*Advertisements*

Number	Price each	
2	\$25.00	\$50.00
3	15.00	45.00
Total . . . . .		\$95.00

*Wiley's Principles and Practice of Agricultural Analysis*

Number	Price each	
11	\$10.00	\$110.00
3	8.00	24.00
9	7.00	63.00
1	7.50	7.50
1	6.60	6.60
1	6.21	6.21
Total . . . . .		\$217.31

*Dues*

1932 dues from institutional members, 44 at \$5.00 . . . . . \$220.00

*Reprints*

Wm. F. Kunke, Oak Park, Ill. . . . .	\$4.40
N.J. Agricultural Expt. Station, New Brunswick, N.J. . . . .	5.15
New York Sugar Trade Laboratory, New York, N.Y. . . . .	7.00
University of Nebraska, Lincoln, Neb. . . . .	4.40
Purdue University, Lafayette, Ind. . . . .	14.75
Conn. Agricultural Expt. Station, New Haven, Conn. . . . .	2.60
Research Corporation, New York, N.Y. . . . .	1.15
Dept. of Agriculture, St. Paul, Minn. . . . .	5.25
University of California, Berkeley, Calif. . . . .	3.00
Boyce Thompson Institute, Yonkers, N.Y. . . . .	8.60
Research Corporation, New York, N.Y. . . . .	2.10
S. Alfend, St. Louis, Mo. . . . .	2.40
Earl P. Clark, Washington, D. C. . . . .	3.95
Dept. of Agriculture, St. Paul, Minn. . . . .	5.15
Agricultural Expt. Station, New Brunswick, N.J. . . . .	4.60
Research Corporation, New York, N.Y. . . . .	2.00
University of California, Berkeley, Calif. . . . .	5.35
University of Kentucky, Lexington, Ky. . . . .	9.00
University of Tennessee, Knoxville, Tenn. . . . .	2.60
Macdonald College, Quebec, Canada . . . . .	7.80
F. A. Vorhes, Washington, D.C. . . . .	3.40
Rhode Island State College, Kingston, R.I. . . . .	4.00
Total . . . . .	\$108.65

*Miscellaneous*

Books ordered through Association .....	\$16.56
Interest on bonds .....	33.75
Transfer of funds .....	\$2,000.00
Total .....	\$2,050.31

Total for Methods, Journals, Wiley books, Advertisements, Reprints, Dues and Miscellaneous .....	\$8,958.01
Cash in bank, October 1st, 1932 .....	5,834.30

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\$14,792.31

## DISBURSEMENTS

*Federal-American National Bank and Trust Company*

1932			Checks
Sept. 19	Maruzen Company Ltd., Japan, refund on sub- scription .....	\$2.20	468
20	The Postmaster, Washington, D.C., box rent. . .	2.00	471
Oct. 17	Leavitt-Ferguson Co., refund on methods. . . .	5.00	472
17	J. J. Betton, interest on bond for M. A. Bates	5.00	473
17	Geo. Banta Publishing Co., storage, Journals	3.00	474
17	Geo. Banta Publishing Co., reprints, 16, 3. .	49.69	475
20	C. C. Todd, for old copies of Journal. . . . .	12.00	476
Nov. 8	M. A. Bates, office expenses. . . . .	50.00	477
9	W. F. Roberts Co., Wiley Circular . . . . .	31.75	478
9	Geo. Banta Publishing Co., November Journal. .	1,023.66	479
14	Chemical Publishing Co., Wiley book. . . . .	6.21	480
Dec. 6	H. F. Warneson & Co., binding Journals. . . . .	6.00	481
7	W. F. Roberts Co., letterheads. . . . .	15.75	482
7	John Wiley & Sons, book. . . . .	2.09	483
22	Dr. F. E. Denny, expenses incidental to meeting.	16.28	484
28	Postmaster, Washington, D.C. box rent. . . . .	2.00	485
28	M. A. Bates, cash for stamps . . . . .	50.00	486
Jan. 4	Geo. Banta Publishing Co., insurance on stock. .	11.05	487
4	Geo. Banta Publishing Co., errata slips. . . . .	27.10	488
19	Montgomery Mutual Bldg. & Loan Assoc. . . . .	2,000.00	489
21	Geo. Banta Publishing Co., reprints, 16, 4. . . .	95.66	490
23	Cash, salary for Rose Kennedy. . . . .	15.00	491
23	M. A. Bates, cash for stamps and office expenses.	50.00	492
23	Noel, Few and Co., bond. . . . .	2,008.02	493
31	Rose Kennedy, salary. . . . .	15.00	494
Feb. 7	Geo. Banta Publishing Co., storage on books. . .	3.13	495
7	Chemical Publishing Co., Wiley books. . . . .	333.33	496
7	Rose Kennedy, salary. . . . .	15.00	497
14	Rose Kennedy, salary . . . . .	30.00	498
15	Commercial National Bank, safe deposit box. .	2.75	499
15	Geo. Banta Publishing Co., freight on Methods. .	42.38	500

Mar. 1	P. Blakiston's Sons & Co., book . . . . .	4.80	501
1	M. A. Bates, cash for stamps . . . . .	50.00	502
1	Marian E. Lapp, transfer of funds to Lincoln Nat. Bank . . . . .	2,000.00	503

*Lincoln National Bank*

Mar. 17	Hobson & Company, Treasury Bond . . . . .	1,003.25	1
21	Rose Kennedy, salary . . . . .	30.00	2
22	Postmaster, box rent . . . . .	2.00	3
22	McGraw-Hill Book Co., book . . . . .	3.33	4
30	J. J. Betton, premium on bond, M. E. Lapp . . . . .	5.00	5
30	Geo. Banta Publishing Co., Journal, 16, 1 . . . . .	794.70	6
April 4	Rose Kennedy, salary . . . . .	30.00	7
4	M. A. Bates, office expenses . . . . .	50.00	8
18	Geo. Banta Publishing Co., reprints, 16, 1 . . . . .	84.75	9
18	Rose Kennedy, salary . . . . .	30.00	10
May 2	Rose Kennedy, salary . . . . .	30.00	11
15	M. A. Bates, office expenses . . . . .	50.00	12
15	Chemical Publishing Co., Wiley Book . . . . .	6.15	13
15	Geo. Banta Publishing Co., storage on Methods . . . . .	4.00	14
19	Charles C Thomas, publishers, book . . . . .	2.35	15
May 29	Postmaster, payment on 5000 envelopes . . . . .	17.00	16
29	Postmaster, balance on 5000 envelopes . . . . .	100.00	17
June 7	Geo. Banta Publishing Co., Journal, 16, 2 . . . . .	770.07	18
7	Moore-Cottrell Agency, refund on subscription . . . . .	2.20	19
July 15	Ace Letter Service, billheads . . . . .	8 50	21
15	Chemical Publishing Co., Wiley Book . . . . .	6.51	22
15	Geo. Banta Publishing Co., reprints, 16, 2 . . . . .	103.64	23
15	M. A. Bates, stamps and office expenses . . . . .	50.00	24
Aug. 15	John Wiley & Sons, book . . . . .	1.51	25
15	Joseph Cohen, affidavits . . . . .	10 00	26
17	Charles L. Parsons, rebate on subscription . . . . .	1.00	27
29	Geo. Banta Publishing Co., Journal, 16, 3 . . . . .	850.56	28
29	Geo. Banta Publishing Co., storage on Methods . . . . .	4.00	29
29	P. Blakiston's Son & Co., book . . . . .	8.14	30
Sept. 13	Geo. Banta Publishing Co., postage on Journal . . . . .	5.99	31
13	Ace Letter Service, registration cards . . . . .	3.75	32
13	Bastian Bros. Co., 500 name bars, for meeting . . . . .	30.38	33
18	M. A. Bates, office expenses . . . . .	50.00	34
18	M. A. Bates, stamps for programs . . . . .	20.00	35
22	The Postmaster, box rent . . . . .	2.00	36
22	John Wiley & Sons, book . . . . .	4.51	37
Total . . . . .		\$12,161.14	
Cash in bank October 1st, 1933 . . . . .		2,631.17	
		<hr/>	
		\$14,792.31	

## OPERATING ACCOUNT

Commercial National Bank

## RECEIPTS

1932			
Oct. 1	Bank balance.....	\$328.38	
	1932 dues from institutional members, 5 at \$5.00.	25.00	
			<hr/>
			\$353.38

## DISBURSEMENTS

1932			Check
Oct. 5	W. F. Roberts Co., programs.....	\$72.50	96
Oct. 20	M. A. Bates, expenses 1932 meeting.....	40.00	97
	Tax on checks.....	.06	
			<hr/>
		112.56	

1933			
Oct. 1	Cash in bank.....	240.82	
			<hr/>
	Total.....		\$353.38

## SUMMARIZED STATEMENT

Bank balance.....	\$2,631.17
Savings (Montgomery Mutual Bldg. & Loan Assoc.)...	3,276.46
Treasury gold certificates.....	\$4,000.00
	<hr/>
Total.....	\$9,907.63

In addition to this cash balance we have an inventory, as stated in the separate reports, of approximately 2500 *Methods*, 30 copies of *Wiley's Principles and Practice* and 13000 copies of back numbers of *The Journal*.

Approved.

W. W. SKINNER

REPORT OF COMMITTEE TO COOPERATE WITH OTHER  
COMMITTEES ON FOOD DEFINITIONS

This Committee respectfully submits the following report.

But one meeting was held during the year, this, the 43rd, occurring during the period April 3-12.

The Committee gave public hearings on the following topics: alimentary pastes, lemon oil, apple butter, and dried fruits. Informal conferences with representatives of the trade were also held on molasses and carbonated beverages, and consideration was given to a schedule of definitions for the latter supplementary to those already established, and inclusive of such "sodas" as orange, lemon, and lime. Because of certain questions arising, it was decided to defer action on these definitions.

Tentative definitions were prepared for grades of molasses, to be designated as "New Orleans," or "table," and as "cooking," provision being made in these for limitations as to the moisture and ash content and for minimum contents of total sugars.

Tentative definitions were also formulated for eggs in the various forms appearing upon the market, these being inclusive of whole, liquid, frozen and dried; also normal, frozen and dried egg yolks.

Consideration was given to acidophilus milk and to heavy tomato purée and chili sauce, but no affirmative action was taken on either of these items.

The standards contained in the existent definition for lemon oil were deleted, the definition for this product as revised and given final adoption being as follows:

*Oil of lemon* is the volatile oil expressed, without the aid of heat, from the fresh peel of the lemon (*Citrus lemonia* Osbeck), with or without previous separation of the pulp and peel.

Numerous trade requests having been received for modifications of the definitions for alimentary pastes, and it appearing from due consideration that certain changes in this schedule were warranted, the following revision was made and given final adoption:

*Macaroni* is the shaped and dried doughs prepared by adding water to one or more of the following: semolina, farina, wheat flour. It may contain added salt. In the finished product the moisture content does not exceed 13 per cent. Various shapes of macaroni are known under distinguishing names, such as spaghetti, vermicelli.

*Semolina Macaroni* is macaroni in the preparation of which semolina is the sole farinaceous ingredient.

*Farina Macaroni* is macaroni in the preparation of which farina is the sole farinaceous ingredient.

*Noodles, Egg Noodles*, are the shaped and dried doughs prepared from wheat flour and eggs, with or without water, and with or without salt. The egg ingredient may be whole egg and/or egg yolk. In the finished product the moisture content does not exceed 13 per cent; and the egg content, upon the moisture-free basis, is not less than 5.5 per cent by weight of egg, calculated as whole egg solids. Noodles are commonly ribbon-shaped.

*Plain Noodles* are the shaped and dried doughs prepared from wheat flour and water, with or without salt. In the finished product the moisture content does not exceed 13 per cent. Plain noodles are commonly ribbon-shaped.

Final adoption was given to the following definition and standard for apple butter:

*Apple Butter* is the semi-solid product obtained by cooking to a suitable consistency the strained edible portion of apples with sugar and/or dextrose, with or without one or more of the following: apple juice, boiled cider, spice, salt. In its preparation not less than 5 parts by weight of the strained apples are used to each 2 parts by weight of sugar and/or dextrose. The product has a characteristic apple flavor and is commonly spiced.

The following schedule of definitions for dried fruits received final adoption:

*Evaporated Apples* are peeled, cored, and sliced apples from which the greater



portion of the moisture has been evaporated. The finished product contains not more than 24 per cent of moisture.

*Dried Apricots* are halved and pitted ripe apricots from which the greater portion of the moisture has been evaporated. Before packing, the dried fruit is commonly processed by washing. The finished product contains not more than 26 per cent of moisture.

*Dried Peaches* are halved and pitted ripe peaches from which the greater portion of the moisture has been evaporated. Before packing, the dried fruit is commonly processed by washing. The finished product contains not more than 26 per cent of moisture.

*Dried Prunes* are whole, ripe prune plums from which the greater portion of the moisture has been evaporated. Before packing, the dried fruit is commonly processed by treatment with boiling water or steam. The finished product contains, in the fleshy portion, not more than 25 per cent of moisture.

C. D. HOWARD  
E. M. BAILEY  
G. G. FRARY

Approved.

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No report was made by the Committee on Sampling.

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No report was made by the Committee on Bibliography.

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#### REPORT OF AUDITING COMMITTEE

The Auditing Committee has examined the accounts of the secretary-treasurer of the Association of Official Agricultural Chemists and the accounts of the same official for *The Journal* of the Association, and for *Methods of Analysis* and *Wiley's Principles and Practice*, from October 1, 1932 to October 1, 1933, and find the same correct.

R. W. FREY  
L. S. WALKER

Approved.

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#### REPORT OF COMMITTEE ON NECROLOGY

Two deaths are to be reported among the membership of our Association since the previous meeting of November, 1932. The first of these is that of Ernest R. Smith, Chief of the St. Louis Station of the U.S. Food and Drug Administration, which occurred on December 30, 1932, following an operation for appendicitis. He was 45 years of age.

Although not a frequent attendant at our meetings Mr. Smith took a deep interest in the work of the Association. He was the author, with Samuel Alfend and Lloyd C. Mitchell, of a most painstaking report on the "Detection of Added Pepper Shells in Pepper," which was presented at the 41st annual convention of the Association in October, 1925, and

published in Vol. 9 of *The Journal* (pp. 333-342). The following obituary notice of Mr. Smith, in the Food and Drug Review for February, 1933, is reproduced herewith:

Mr. Smith received the Ph.C. degree from the University of Kansas in 1912 and in 1917 the degree of LL. B. from the Kansas School of Law. He worked as a chemist for a drug concern for one year and then entered the service of the city government of Kansas City as a food and drug inspector. He was then assigned chemical and bacteriological work for the Kansas City Board of Health, devoting much time to the examination of water, milk and other food products.

He was appointed in 1917 as a food and drug inspector at the Kansas City Station, and after preliminary training was transferred to the Cincinnati Station. Two years later he was placed in charge of the inspection work at Kansas City and, in 1920, just a little more than three years after entering the service, he was appointed Chief of the St. Louis Station, a position he filled with marked ability until his death. His training and experience fitted him exceptionally well both for the work of a food and drug inspector and for that of a station chief.

Mr. Smith, on December 11, 1932, was operated on for appendicitis. Complications set in and his condition became critical. After ten days he seemed to improve, and it was generally believed he was well on the road to recovery. The latter part of the month he had a relapse. His condition again became critical. Arrangements were made for a blood transfusion, every one at the office volunteering for the service. He died on the morning of December 30. The autopsy showed death was due to gangrene.

Mr. Smith was engaged to be married, and but for his illness and death the wedding would have taken place during the holidays.

Funeral services were held on January 1 in St. Louis with interment at Hartford, Kansas.

The other death to be mentioned is that of Samuel W. Wiley, President of the firm of Wiley and Co., consulting chemists of Baltimore, which occurred on February 23, 1932, and was overlooked in our necrology of last year.

Dr. Wiley was born at Amherst, Mass., on March 17, 1879. He graduated from the Massachusetts Agricultural College of Amherst in 1898 and worked for the next four years as chemist of the Massachusetts Agricultural Experiment Station. He was engaged as chemist for the fertilizer industry from 1902 to 1906, when he went into private consulting practice in Baltimore. In 1925 he obtained the degree of Doctor of Science from Washington College. He took an active part in the work of various civic and fraternal organizations, was a member of the American Chemical Society, American Oil Chemists Association and other scientific bodies, and although not a contributor to the work of our Association was a constant attendant at its meetings for many years. He will be long remembered for his genial personality and for the strong interest which he always showed in the work of our Society.

I move you, Mr. President, that we all rise as a token of respect to the memory of these, our lamented coworkers.

Approved

C. A. BROWNE, *Chairman*

*J. W. Kellogg:* Before calling for the report of the Committee on Nominations I desire to express to you my appreciation of your fine cooperation and for the honor conferred upon me. I appreciate the resolutions of the report not only for myself but especially for other officers. It was a great source of joy to be of service to you. I have learned a great deal coming to these meetings. We help to coordinate our ideas in a coalesced line of procedure. How we have similar experiences and see differently makes me think of a story. Four years ago four men of four different nationalities went hunting elephants in Africa. There was an Englishman, a Frenchman, a German and an American. They had the same kind of guns and bullets, and the elephants they hunted were of the same species, same type; there was no variation at all in any of their experiences. After the hunt they returned home to their respective countries and wrote theses on the elephant. The Englishman wrote on the "Conservation of the Elephant," the German on the "Origin and Species of the Elephant," the Frenchman on the "Love Affairs of the Elephant," and the American, "How to Get Bigger and Better Elephants."

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#### REPORT OF NOMINATING COMMITTEE

The Committee on Nominations submits the following report:

*President:* R. Harcourt, Guelph, Canada

*Vice-President:* F. C. Blanck, Washington, D. C.

*Secretary-Treasurer:* W. W. Skinner, Bureau of Chemistry and Soils, Washington, D. C.

*Additional Members of the Executive Committee:*

H. H. Hanson, Dover, Del.

C. C. McDonnell, Washington, D. C.

H. R. Kraybill, Lafayette, Ind.

*Post-officio,*

J. W. Kellogg, Harrisburg, Pa.

G. S. FRAPS

F. P. VEITCH

W. H. MACINTIRE

A unanimous vote was cast for the officers nominated.

H. A. Lepper was appointed as a member of the Board of Editors in place of F. C. Blanck, whose term of office had expired, and L. E. Bopst was appointed in place of R. N. Brackett, retired, on the Committee on Definitions of Terms and Interpretation of Results on Fertilizers and Liming Materials and also on the Committee on Sampling.

*J. W. Kellogg:* I'll ask the Nominating Committee to escort Mr. Harcourt to the Chair.

It gives me great pleasure to transfer the gavel to you as President of this Association.

*R. Harcourt:* I want to thank you for the honor you have done me in appointing me to this position. I am sure you have taken this action to recognize the Canadian group rather than to recognize this particular Canadian. I can only say that I shall do the best I can under the guidance of the Secretary, Dr. Skinner, and Miss Lapp. I think if I follow their guidance I'll not come out too badly at the end of the year.

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### REPORT OF COMMITTEE ON RESOLUTIONS

*Whereas*, the present Federal food and drugs act has been of inestimable value to the American public in protecting it from adulterated and misbranded foods and drugs, and whereas due to modern developments of manufacture, distribution and advertising of foods and drugs, revision of the Act is necessary in order to maintain and increase such protection, therefore be it resolved that we, members of the Association of Official Agricultural Chemists, (1) express our approval of the principles involved in the proposed revision of the Federal food and drugs act now before Congress, and (2) urge that all members of our Association actively support the enactment of the objectives of this revision, and (3) that a copy of this resolution be sent to the Secretary of Agriculture and the chairmen of the appropriate committees of Congress considering this new legislation.

*Whereas*, the Association of Official Agricultural Chemists is organized for the purpose of developing new and improved methods of analysis applicable to regulatory, research and industrial use in the field of agricultural chemistry, and whereas this Association, by its publications and the type of work which it is undertaking has established an enviable reputation in these fields, and whereas this Association is a non-profit organization and consequently is limited in the extent to which its publication and research activities can be developed, therefore be it resolved that the President appoint a committee to study the problem of interesting one or more foundations with educational and welfare objectives in providing a permanent endowment, the interest on which shall be devoted to the various activities of this Association.

*Resolved:* That this Association extend to Dr. Alfred R. L. Dohme, its sincere appreciation of his interesting Wiley Memorial Address on "The History and Value of Germicides."

*Resolved:* That this Association extend to the management of the

Raleigh Hotel a vote of thanks for the accommodating manner with which it has served us and for the many courtesies which have been extended to our members and friends at this meeting.

*Resolved:* That this Association favors the appointment of official delegates to attend the Third International Congress of Chemists and Technologists for Agricultural Industries to be held in Paris in the spring of 1934.

F. C. BLANCK  
C. S. CATHCART  
W. B. WHITE

Approved.

## CONTRIBUTED PAPERS

### THE EQUIVALENT PHYSIOLOGICAL ACIDITY OR BASICITY OF AMERICAN FERTILIZERS<sup>1</sup>

By ARNON L. MEHRING and AVIS J. PETERSON (Fertilizer Investigations, Bureau of Chemistry and Soils, U. S. Department of Agriculture, Washington, D. C.)

Certain fertilizer materials, although neutral in reaction themselves, have long been known to change the reaction of the soil to which they are applied. They are termed "physiologically acid" or "physiologically basic." Until recent years fertilizer mixtures were believed to be practically neutral in their effect on soil reaction because as a rule they contained both acid and base-forming ingredients. In the last few years, however, the greatly increased use in mixed fertilizers of ammonium salts, which are physiologically very acid has presumably rendered the present average mixed fertilizer acid in its effects upon the soil.

More fertilizer is applied to the soils of the Atlantic Coastal Plain than to those of any other section. Cooper reported at the Fall Meeting of the American Chemical Society in 1933 that approximately 33 per cent of such soils examined in South Carolina were more acid than pH 5.0 and that 4 per cent were more acid than pH 4.5. Very few economic plants will produce high yields in soils with an acidity greater than pH 5.0. It is therefore important not to use fertilizers that will increase the acidity of soils already strongly acid, and it would be of interest to know what effect the average mixed fertilizer really has on soil reaction.

It is the purpose of this paper to give in terms of the calcium carbonate equivalent the calculated amount of acidity or basicity likely to be produced from the fertilizers used in this country as a whole, as well as in several states, and to point out the changes that have occurred in this respect since mixed fertilizers came into general use.

#### METHODS AND RESULTS

The amount of acid or base developed in the average soil by various materials in terms of equivalents of calcium carbonate per unit of plant food was recently worked out by Pierre.<sup>2</sup> His equivalents were employed with data given by Mehring and Peterson<sup>3</sup> on the composition and tonnage of materials used in fertilizers to calculate the average physiological reaction of the mixed fertilizers produced in certain years in the United States. The numbers of units of each plant food were determined from the tonnage and average composition of the materials used in making

<sup>1</sup> Presented at the Annual Meeting of the Association of Official Agricultural Chemists, held at Washington, D. C., November, 1933.

<sup>2</sup> *Ind. Eng. Chem. Anal. Ed.*, 5, 229-34 (1933).

<sup>3</sup> U. S. Dept. Agr. Circ. 315 (1934).

mixed fertilizers, and these numbers were multiplied by the appropriate equivalents given by Pierre to determine the amount of acid or base produced. The results are presented in Table 1.

It will be noted that in 1900 and 1905 the fertilizers produced were basic in effect. Those manufactured from 1909 to 1919 were slightly acid, but since 1925 they have increased in physiological acidity at a rapid rate.

The chloride and sulfate of potash appear from the review given by Burgess<sup>1</sup> to have no consistent effect upon soil acidity. Pierre gives no equivalents for these or any other potash materials, except the nitrate. Wood ashes and potassium carbonate are decidedly alkaline in their effect, however, and it was therefore decided to include them in these

TABLE 1.

*Equivalent acidity and basicity of fertilizers produced from 1900 to 1931*

YEAR	EQUIVALENT BASICITY	EQUIVALENT ACIDITY
	<i>lbs. CaCO<sub>3</sub> per ton</i>	
1900	39.74	—
1905	36.82	—
1909	—	16.37
1913	—	22.93
1917	—	18.95
1919	—	15.72
1925	—	40.09
1929	—	127.69
1931	—	161.27

calculations. The theoretical basic equivalent of 21 pounds of calcium carbonate per unit of K<sub>2</sub>O was used, and it was found that owing to the small tonnage of such materials their effect on the final result was only a few pounds per ton.

The superphosphates and principal carriers of potash are essentially neutral in their average effects upon soils. Those materials supplying phosphoric acid or potash exclusively that are not neutral are used in such small quantities that their effects are insignificant. It therefore appears justifiable to calculate the effects of mixed fertilizers upon soils from the content of nitrogen in its various forms. The percentage of nitrogen so found is reported by a number of the state control laboratories. These figures were averaged and used to calculate the physiological reaction of mixed goods consumed in the states reporting. This is conceded to be a less accurate method than the one previously mentioned, but it is the only available way to get such information for individual states, and

<sup>1</sup> Rhode Island Agr. Expt. Sta. Bull. 189 (1922).

when used with average figures for the country as a whole it gave results that checked very well with those obtained by the previous method.

In Table 2 are given the average percentages of the different forms of nitrogen found by analysis in the complete mixed fertilizers in certain states in 1932. These were determined from analyses published in state fertilizer control reports with two exceptions, those for North Carolina and West Virginia, which were very kindly supplied in private communications by C. B. Williams for North Carolina and by W. H. Pierre for West Virginia.

According to Pierre one unit of nitrogen in the form of ammonia liquor, ammonium phosphates and ammonium sulfate is equivalent to 36, 104

TABLE 2

*Different forms of nitrogen used in mixed fertilizers in various states in 1932 and their equivalent acidities*

STATE	FORM OF NITROGEN				EQUIVALENT ACIDITY
	AMMONIUM SALTS	NITRATES	ORGANIC AMMONIATES	CYANAMID AND UREA	
	per cent	per cent	per cent	per cent	lbs. $\text{CaCO}_3$ per ton
California	2.69	.90	3.35	—	206
Connecticut	2.99	.64	1.09	.44	224
Maine	3.36	.43	.57	.48	263
Maryland*	2.30	.25	.74	.18	189
Massachusetts	3.10	.70	1.21	.55	226
North Carolina	1.29	.22	.58	.45	86
New Jersey	2.72	.46	.59	.30	213
Oregon	3.44	.32	.45	—	298
West Virginia	2.28	.17	.70	.16	201
United States	2.09	.52	.68	.42	149

\* 1931

and 107 pounds of calcium carbonate, respectively. No statistics are available as yet on the quantities of these materials used in mixed goods in 1932, but for 1931 the figures were 66,803 tons of nitrogen in the form of ammonium sulfate, 20,761 tons in the form of ammonia gas and liquor, and 5,181 tons as phosphates. Thus for 1932 an acidity equivalent of 90 was considered to be about right for ammoniacal nitrogen. In the class of water-soluble organic nitrogen a basicity equivalent of 48 pounds per unit was used because roughly it is the weighted average for the materials in this class. In the same way basic equivalents of 36 and 1 pound of calcium carbonate per ton were employed for each one per cent of nitrogen in the form of nitrates and organic ammoniates, respectively. The net difference between the acid and basic constituents thus calculated is shown in the last column of Table 2. Unfortunately more or less



complete data on the kind of nitrogen present in fertilizer mixtures could be obtained for a few states only. Most of the state fertilizer officials, however, report inorganic and organic, or water-soluble and water-insoluble nitrogen. These figures were arbitrarily divided after careful study of pertinent facts available for each state, such as the statistics of the Department of Agriculture on the amount of cottonseed meal used in mixed goods, the imports of sodium nitrate, etc. These figures were averaged on a tonnage basis with those given in Table 2 to find a weighted average for the United States. These figures for the other states are not presented because they undoubtedly contain errors, but if too much of the sodium nitrate imported into one state was assigned to the nitrate nitrogen of that state and not enough to another state farther from the coast it would make no particular difference in the weighted average for the United States.

The results indicate that the mixed goods consumed in North Carolina, while decidedly acid in effect upon soil, are much less acid than those of the other states included in this work, all of which use fertilizers of greater equivalent acidity than average for the United States. That only one is below average in the table is due to the fact that, although a very large tonnage of the sort of fertilizers used in North Carolina is also used in a number of other states, these data were not given because they are not complete.

The calculations described were repeated for a considerable number of years to obtain information on the changes that have occurred during the past and also on the present trend. Naturally, the states for which the necessary data were available changed from year to year, but relatively more states published complete analyses on the three principal forms of nitrogen in the earlier years than in recent ones. An acid equivalent of 107 was used for ammoniacal nitrogen for the years 1880 to 1927, inclusive. For 1928 this equivalent was given a value of 105 for reasons already assigned in the discussion of figures for 1932. For 1929, 1930 and 1931 it was 100, 95, and 90, respectively. A basic equivalent of 36 was used throughout for nitrate nitrogen because this is Pierre's figure for sodium nitrate, which has always been the source of practically all nitrogen in this form. A different figure for insoluble organic nitrogen was used for each year because so many different materials enter into this category and the kind and proportion are constantly changing. A basic equivalent of 28, the average of the equivalents for the materials used then, was employed for 1880. For 1900 and all years since, weighted averages were prepared from the tonnage of such materials used. These equivalents were all basic, and they varied from 23 in 1900 to 8 in 1925 and 1 in 1931. Cyanamid was the only material exclusively supplying water-soluble organic nitrogen from 1915 to 1927, and, therefore a basic equivalent of 57 was used for this class in these years. A value of 55 was assigned for 1928 because of the

appearance of urea, and this was further decreased to a basicity equivalent of 48 for recent years because of the increased use of urea and calcium urea.

From 1880 to 1905 the average mixed fertilizer appears from the results in Table 3 to have been basic in its effects. From 1907 to 1924 it was slightly acid, and since then it has been increasing rapidly in acidity, although during the last few years the trend is no longer sharply upward.

TABLE 3

*Different forms of nitrogen used in mixed fertilizers and the resultant equivalent acidities or basicities*

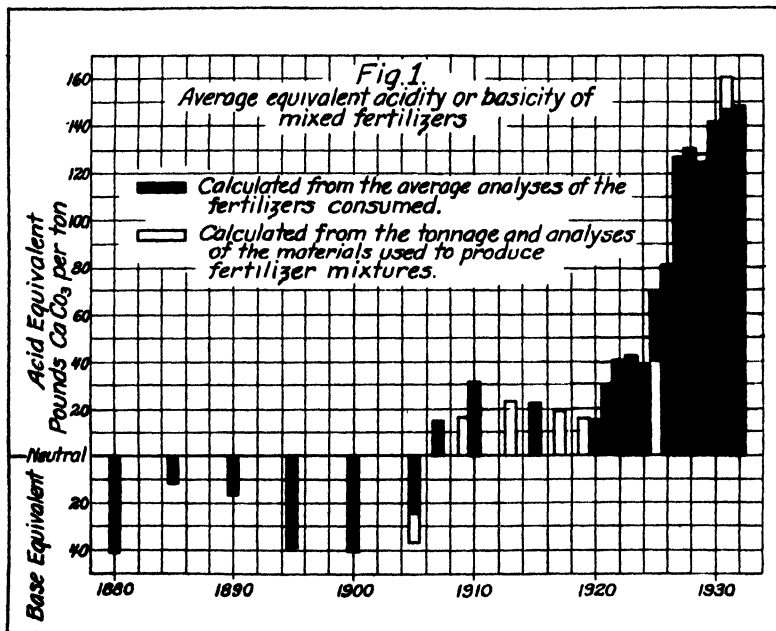
YEAR	FORM OF NITROGEN				EQUIVALENT BASICITY	EQUIVALENT ACIDITY
	AMMONIUM SALTS	NITRATES	ORGANIC AMMONIATES	CYANAMID AND UREA		
	per cent	per cent	per cent	per cent	lbs. CaCO <sub>3</sub> per ton	lbs. CaCO <sub>3</sub> per ton
1880	.18	.09	2.03	—	40.82	—
1885	.42	.12	1.86	—	11.5	—
1890	.34	.18	1.84	—	16.1	—
1895	.18	.43	1.79	—	39.2	—
1900	.12	.49	1.48	—	38.8	—
1905	.22	.54	1.40	—	23.9	—
1907	.47	.43	1.25	—	—	14.8
1910	.60	.42	1.26	—	—	31.4
1915	.53	.50	1.06	.07	—	22.0
1920	.54	.65	.82	.19	—	15.4
1921	.65	.56	.81	.22	—	28.8
1922	.78	.63	.82	.22	—	40.0
1923	.78	.57	.89	.23	—	41.8
1924	.81	.69	.97	.24	—	39.4
1925	1.06	.61	.86	.25	—	70.3
1926	1.14	.53	.99	.26	—	81.2
1927	1.50	.38	.79	.27	—	127.4
1928	1.55	.40	.77	.28	—	130.6
1929	1.59	.46	.70	.35	—	124.2
1930	1.80	.42	.81	.26	—	141.8
1931	1.93	.39	.79	.25	—	146.9
1932	2.09	.52	.68	.42	—	148.5

The two sets of data calculated from production and from analyses are plotted together in Fig. 1, and it will be seen that they tend to confirm each other.

#### DISCUSSION

In the earlier paper to which reference has been made, the writers show that about 300 pounds of filler is used on the average in preparing a ton of mixed fertilizer. It has been estimated that 25 to 30 pounds of this

amount already consists of liming materials. This proportion leaves more than sufficient leeway to produce physiologically neutral fertilizers if the sand ordinarily used is replaced in whole or in part by dolomite or limestone, because on the average it requires only 150 pounds of pure limestone to do this. The only difference in retail price should be the difference in the wholesale cost of sand and the liming material, which in most localities would be a very small sum per ton of mixed fertilizer, because the cost of mixing, bagging, freight, and handling is identical in both cases.



It is highly desirable that the purchaser should have means of knowing whether the fertilizer he considers buying is acid, neutral or basic, so that he may make his purchase intelligently, and the control official should have some method of protecting him.

#### SUMMARY

Calculations show that from 1880 to 1906 the average equivalent physiological effect of mixed fertilizers on soil reaction was basic; from 1907 to 1924 it was slightly acid; and since then the acidity has increased rapidly, until in 1932 it was equivalent to 150 pounds of calcium carbonate per ton of fertilizer. At the present time the upward trend appears to have been checked.

The present acidity could be more than neutralized when desirable by substituting dolomite or limestone for sand in the analysis formula at very little additional cost to the consumer.

## THE EQUIVALENT ACIDITY AND BASICITY OF FERTILIZERS AS DETERMINED BY A NEWLY PROPOSED METHOD<sup>1</sup>

By W. H. PIERRE (Department of Agronomy and Genetics, West Virginia University, Morgantown, W. Va.)

During the last few years there has been a rapidly growing interest in the use of limestone supplements, particularly the use of dolomitic limestone, as filler in mixed fertilizers. The reason for this is twofold. In the first place there has been a gradual recognition of the acid-forming property of mixed fertilizers and of the value of limestone fillers to correct this condition, and, secondly, it has been shown by various investigators<sup>2</sup> that the use of magnesium compounds such as dolomitic limestone has a beneficial effect on many soils.

Until recently it was generally believed that the use of limestone in mixed fertilizers would result in materially decreasing the availability of the phosphate, and also in a loss of ammonia from certain ammonium compounds. The recent investigations of MacIntire and his associates,<sup>3</sup> and of Ross<sup>4</sup> have shown, however, that while under some conditions the use of a high calcium limestone may result in losses of available phosphoric acid and of ammonia, such losses are negligible or nil if dolomitic limestone is used.

The importance of using dolomitic limestone as filler in mixed fertilizers has been adequately emphasized by Parker<sup>1</sup> and by MacIntire.<sup>2</sup> It suffices to state here that dolomitic limestone supplements serve two primary functions: First, they supply calcium and magnesium, both of which are important constituents of fertilizers, and second, they reduce or completely neutralize the residual acidity left in soils by acid-forming fertilizers. As limestone is, therefore, a desirable constituent of fertilizers sold in the heavy-consuming sections of eastern United States, it is evident, as pointed out by Parker,<sup>5</sup> that its use should be encouraged, and that proper credit should be given for limestone supplements used in the production of non-acid-forming fertilizers. This investigator emphasized further that the use of limestone should be subject to control dependent upon analysis, as is the case with nitrogen, phosphoric acid, and potash, and that a method should be worked out in order to make such chemical control possible. MacIntire<sup>6</sup> has likewise emphasized the need of perfect-

<sup>1</sup> Presented at the meeting of the Fertilizer Section of the American Chemical Society, Chicago, Ill., September, 1933, and at the Annual Meeting of the Association of Official Agricultural Chemists, Washington, D. C., November, 1933.

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"Equivalent acidity" is defined as the acidity developed by a fertilizer when applied to soils, measured in terms of calcium carbonate required for its neutralization. "Equivalent basicity" is defined as the basic residue left in soils by fertilization expressed as equivalent calcium carbonate.

<sup>2</sup> Jones, *J. Agr. Research*, 39, 873 (1929); Chucks, *J. Am. Soc. Agron.*, 23, 1052 (1931); Cooper, *South Carolina Expt. Sta. Ann. Rpts.* 36 and 38 (1931).

<sup>3</sup> MacIntire and Sanders, *J. Am. Soc. Agron.*, 30, 764 (1928); MacIntire and Shuey, *Ind. Eng. Chem.*, 24, 933 (1932); MacIntire and Shaw, *Ind. Eng. Chem.*, 24, 1401 (1932).

<sup>4</sup> Ross, Paper presented at American Chemical Society meeting, Chicago, September, 1933.

<sup>5</sup> *Am. Fert.*, Jan. 16 (1932).

<sup>6</sup> *This Journal*, 16, 589 (1933).

ing a workable method for controlling the use of limestone supplements.

During the past year the writer has been working on such a method. As the method developed has been published in detail,<sup>1</sup> only the principles upon which it is based will be given. The primary object of this paper is to present some data regarding the accuracy and adaptability of the method, as obtained first by a study of fertilizers of known equivalent acidity and basicity and, second, through a collaborative study with a number of mixed fertilizers.

#### PRINCIPLES OF PROPOSED METHOD

The method consists essentially in determining the excess of basic or acidic elements in the fertilizer. The basic elements involved are calcium, magnesium, sodium, and potassium, and the acidic elements are phosphorus, sulfur, chlorine, and nitrogen. Nitrogen is often present in fertilizers as a cation or base, but as it is readily changed to nitrates in soils through biological action, it must necessarily be considered acidic. If the amount of each of these elements present in a fertilizer were known, the acid- or base-forming character of the fertilizer could be readily calculated. The determination of the eight elements involved according to such a scheme, however, would be tedious and the method would not be adapted to routine work.

The method proposed for determining the equivalent acidity and basicity of fertilizers, although based on the same general principle as that just outlined, is simple and much more rapid. It consists essentially in titrating the excess of acidic or basic elements in the fertilizer after first igniting to destroy the organic matter and to volatilize the nitrogen. Sulfur,\* phosphorus, and chlorides are retained during ignition by the use of sodium carbonate, and some organic matter, such as sugar or carbon black, is added to the sample before ignition in order to help volatilize any nitrates present. The total nitrogen is determined in a separate sample, and the equivalent acidity or basicity of the fertilizer is calculated by taking the algebraic sum of the acidity due to the nitrogen and the acidity or basicity obtained by titration.

#### EQUIVALENT ACIDITY AND BASICITY OF FERTILIZER MATERIALS

*Nitrogenous Fertilizers.*—It is a well-known fact that nitrogenous fertilizers vary considerably in their effect on soil reaction. As the amounts of residual acidity or basicity for a number of nitrogenous carriers are known, it is possible to determine the accuracy of the proposed method by comparing the equivalent acidity and basicity values obtained with it with the known values. The data from such a comparative study are

<sup>1</sup> *Ind. Eng. Chem. Anal. Ed.*, 5, 229 (1933).

\* Some organic sulfur may be lost from the organic carriers, but the loss is such that the error is negligible.

given in Table 1. The equivalent acidity and basicity values obtained by titration are given in the third and fourth columns, and the acidity due to the nitrogen in the fifth column. The equivalent acidity or basicity of these carriers expressed on the ton basis would then be equal to the algebraic sum of the values given in these three columns. As values expressed on the basis of units of nitrogen are more comparable than those expressed on the basis of tons of fertilizer, the equivalent acidity and basicity of these fertilizers per unit of nitrogen are given in the last four columns of the table. The results given in the last and third from the last columns are actual values found in soil fertilization experiments in the case of the more common carriers and theoretically calculated values in the case of the newer nitrogenous fertilizers. It will be noted that the results obtained by the proposed method agree well with the actual, or theoretical, values.

TABLE 1

*Equivalent acidity and basicity of nitrogen carriers ( $\approx$ lbs.  $\text{CaCO}_3$ )*

SOURCES OF NITROGEN	N	TITRATION VALUES		ACIDITY DUE TO N PER T	EQUIVALENT ACIDITY		EQUIVALENT BASICITY	
		ACIDITY PER T	BASICITY PER T		PER UNIT N		PER UNIT N	
	<i>per cent</i>				<i>Found</i>	<i>Calc.</i>	<i>Found</i>	<i>Calc.</i>
Cyanamid	22.0	—	2030	785	—	—	57	50
Sodium nitrate	16.4	—	1168	585	—	—	36	36
Potassium nitrate	13.0	—	979	464	—	—	40	36
Calcium nitrate	15.0	—	943	536	—	—	27	29
Calnitro	16.0	—	917	571	—	—	22	27
Calnitro	20.5	—	726	732	0	—	0	—
Ammonium nitrate	35.0	—	—	1250	—	36	—	—
Urea	46.6	16	—	1664	36	36	—	—
Anhydrous or aqua ammonia	—	—	—	—	—	36	—	—
Nitrophoska	15.0	462	—	536	67	63	—	—
Nitrophoska	10.0	324	—	357	68	63	—	—
Diammophos	21.0	718	—	750	70	71	—	—
Leunaphos	20.0	1152	—	714	93	93	—	—
Ammophosko No. 1	12.0	691	—	428	93	—	—	—
Ammophosko No. 3	10.0	710	—	357	107	—	—	—
Ammophos A	11.0	704	—	393	100	107	—	—
Ammophos B	16.5	1186	—	589	108	107	—	—
Ammonium chloride	26.1	1854	—	932	107	107	—	—
Ammonium sulfate	21.1	1496	—	753	107	107	—	—

*Potassium and Phosphorus Fertilizers.*—As would be expected, the common potassium fertilizers, muriate and sulfate of potash, were found to be practically neutral according to the proposed method. This is in agreement with the results of field experiments in which it has been shown that they have no significant residual effect on soil reaction.

Phosphate fertilizers affect soil reaction differently, depending on whether the compounds are mono-, di-, or tri-basic, and also depending somewhat on the acidity of the soils to which they are applied.<sup>1</sup> With soils of medium to slight acidity, superphosphate can be considered neutral, whereas di- and tri-calcium phosphate are basic. These results are in accordance with those obtained by the proposed method. The values for different samples of superphosphate ranged from an equivalent acidity of 24 pounds equivalent  $\text{CaCO}_3$  per ton to an equivalent basicity of 62 pounds. These minor variations are probably explained by the presence of free acid in the former case and of undecomposed rock phosphate in the latter.

Other phosphate carriers, such as steamed bone meal, Texas bone, precipitated bone, bone ash, and rock phosphate, were found to be basic as determined by the proposed method. This is as would be expected because the phosphates in these compounds are probably largely in the tri-calcium form. With regard to rock phosphate, however, there is a question as to whether its basicity as determined by the proposed method should be allowed because it is known that the reaction of rock phosphate with soils is very slow.<sup>1</sup> If it should not be desirable to allow the total basicity given by rock phosphate, the necessary correction can be readily made on the basis of the content of citrate-insoluble phosphoric acid. Preliminary studies have shown this method of correction to be satisfactory. That part of the equivalent basicity of rock phosphate which would not be allowed can be obtained by multiplying the percentage of citrate-insoluble  $\text{P}_2\text{O}_5$  in the fertilizer by the factor 28.2. Thus, if a sample of rock phosphate has an uncorrected equivalent basicity of 1140 pounds per ton and contains 31.9 per cent citrate-insoluble  $\text{P}_2\text{O}_5$  the corrected equivalent basicity would be  $1140 - (31.9 \times 28.2)$  or 240 pounds per ton. In a similar manner this method of correction can be applied to the citrate-insoluble  $\text{P}_2\text{O}_5$  content of mixed fertilizers.

#### COLLABORATIVE STUDY OF METHOD

In order to determine how accurately results obtained in one laboratory can be duplicated, a set of ten fertilizer samples were sent out to eight fertilizer and soil chemists who kindly offered to collaborate in the study. A description of these fertilizers is given in Table 2. Samples 1C to 4C inclusive were prepared in the laboratory, whereas the last six were commercial mixtures. Samples 1C and 2C were exactly alike except that sand was used as filler in the former and dolomitic limestone in the latter. Samples 3C and 4C were prepared in a similar manner. By comparing the results obtained from 1C and 2C, and from 3C and 4C, it is possible to study the accuracy of the method in determining the amount of lime-

<sup>1</sup> Pierre, *J. Am. Soc. Agron.*, in press (1933).

stone added. Each collaborator received a description of the method and also the results obtained by the writer on two of the samples, Nos. 6C and 7C. The results of the collaborative study are given in Table 3. The average value for each fertilizer is given in the fourth from the last column, and the deviations from the average in the next two columns. It will be noted that the average deviation ranged from 5 to 14 pounds of calcium carbonate per ton, whereas the maximum deviation ranged from 10 to 45 pounds of calcium carbonate. Although the maximum deviations from the average are in a few cases higher than would be desired, the agreement is

TABLE 2.—*Description of fertilizer samples used in collaborative study*

FERT. NO.	ANALYSIS	SOURCES OF NITROGEN AND PERCENTAGE OF NITROGEN FROM EACH SOURCE
1C	4-12-4	Ammonium sulfate 50%; Cyanamid 25%; Urea 25%
2C	4-12-4	Ammonium sulfate 50%; Cyanamid 25%; Urea 25%
3C	5-8-7	Ammonium sulfate 40%; Tankage 20%; Ammophos A 20%; Nitrate of soda 20%
4C	5-8-7	Ammonium sulfate 40%; Tankage 20%; Ammophos A 20%; Nitrate of soda 20%
5C	2-9-5	Ammonium sulfate 50-70%; Ammophos A 10-25%; Tankage 5-15%; Cyanamid 5-10%
6C	4-8-5	Ammonium sulfate 70-90%; Cyanamid 5-10%; Animal Tankage 5-10%
7C	4-12-4	Ammonium sulfate 62.5%; Ammoniated super 25%; Nitrate of soda 10%; Humus 2-5%
8C	4-8-7	Ammonium sulfate 33-50%; Ammonium phosphate 25-33%; Ground tobacco stems 20-25%
9C	5-10-4	Ammonium sulfate 64.7%; Liquid ammonia 21.4%; Nitrate of soda 7.3%; Bean meal 6.6%
10C	4-16-4	Ammonium sulfate 50-70%; Ammophos 15-30%; Nitrate of soda 10-20%

Superphosphate was the source of phosphorus except with samples 3C, 4C, 5C and 10C, where a portion of the phosphate was derived from Ammophos, and 8C where all was derived from Ammophos.

Dolomitic limestone was used as filler in Nos. 2C and 4C, the former at a rate equivalent to 319 lbs. per ton and the latter, 539 lbs.  $\text{CaCO}_3$  per ton.

in general very satisfactory, especially when it is considered that this was the first experience of these different chemists with the method. Moreover, in one case, at least, the collaborator was handicapped by the fact that he did not have a furnace at his disposal for making the ignitions.

In the last column of Table 3 are given the calculated theoretical values for these fertilizers based on a knowledge of the separate ingredients making up the mixture. It will be noted that with samples 1C to 4C, inclusive, a good agreement was obtained between the theoretical values and the average determined value. In the case of the last six fertilizers the calculated values are only approximate, as the exact proportion of the separate ingredients was not definitely known, nor was the value for some of the organic constituents used in some of the fertilizers known. A fair agreement, however, was obtained.



TABLE 3

*Equivalent acidity and basicity of fertilizers as determined by the proposed method\**  
( $\approx$  lbs.  $\text{CaCO}_3$  per ton)

FERT. NO.	HASKIN, MASS.	JONES, VA.	MACHUDER, ROTTER	PARKER, DU PONT	PIERRE, W. VA.	TIDMORE, ALA.	HEESON, U.S.D.A.	BOPERT, MD.	ROBERTSON, S.C.	AVERAGE DEVIATION	MAXIMUM DEVIATION FROM A†.	CALCULATED VALUES†
1C	181A	185A	143A	149A	166A	163A	156A	158A	168A	163A	22	173A
2C	152B	135B	202B	162B	167B	150B	145B	167B	137B	157B	45	146B
3C	220A	177A	197A	187A	209A	184A	206A	214A	209A	200A	23	227A
4C	336B	323B	356B	327B	319B	298B	355B	336B	318B	330B	32	336B
5C	48A	65A	41A	44A	48A	36A	49A	41A	55A	47A	18	71A-144A
6C	277A	275A	263A	279A	266A	263A	282A	273A	278A	273A	10	261A-344A
7C	199A	197A	208A	199A	194A	193A	204A	193A	183A	197A	14	248A
8C	1B	9B	22B	0	12B	17B	2B	7B	10B	9B	13	35B-57A
9C	334A	353A	344A	342A	347A	359A	361A	334A	386A	351A	35	371A
10C	363A	343A	321A	338A	343A	358A	338A	348A	350A	345A	24	313A-371A

\* "A" following figures means "Equivalent Acidity"; "B" following figures means "Equivalent Basicity." See Reference 1 of this paper.

† The calculated values for 5C-10C inclusive are only approximate.

TABLE 4.—*Recovery of added limestone as determined by proposed method\**

COLLABORATOR	SAMPLE 2C		SAMPLE 4C	
	AMOUNT	PERCENTAGE	AMOUNT	PERCENTAGE
Haskins	333	104	556	103
Jones	320	100	500	93
Magruder	345	108	553	103
Parker	311	97	514	95
Pierre	333	104	528	98
Tidmore	313	98	482	90
Beeson	301	94	561	104
Bopst	320	102	550	102
Robertson	305	96	527	98
Average	320	100	530	98

\* The dolomitic limestone added to 2C as filler was equivalent to 319 pounds of calcium carbonate, and to 4C, 539 pounds of calcium carbonate per ton.

The added limestone recovered in Nos. 2C and 4C by the different collaborators is given in Table 4. It will be noted that dolomitic limestone equivalent to 319 pounds of calcium carbonate was added to sample 2C, and that the values determined by the different investigators ranged from 301 to 345 pounds. This means a 94–108 per cent recovery. Likewise, of the 539 pounds equivalent calcium carbonate added to sample 4C, 90–104 per cent was recovered by the different workers, the average per cent recovery being 98.

#### SUMMARY

Further studies were made regarding the accuracy and adaptability of the method proposed for determining the equivalent acidity and basicity of fertilizers. The agreement in results obtained by chemists working in eight different laboratories was found to be satisfactory. Limestone added as filler in mixed fertilizers was accurately evaluated, and all laboratories which were equipped with furnaces for ignition reported that the method was well adapted to routine work.

#### ACKNOWLEDGMENTS

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## METHODS FOR DETERMINATION OF LEAD IN FOODS

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Public health and regulatory food officials have long been aware of the potential danger of relatively minute quantities of lead in foods and of the dearth of rapid and accurate methods for its determination. During the past year the writers made an intensive study of the subject. This paper summarizes the results of this study, which is a contribution to the concerted attempt made by the Department of Agriculture and cooperating agencies to reduce the amount of lead in the form of spray residue by every available means. The principal objective was the determination of lead on sprayed fruits and vegetables, but the principles of the methods described are generally applicable to the determination of lead in other materials, with the possible exception of those in which interfering substances not encountered in spray residues are present. The description of the entire investigation has been coordinated to avoid repetition of features of any method which were carried over to later methods. The accompanying chart indicates the interrelationship of the methods, the alternative procedures that were found satisfactory, and their relationship to methods for the determination of a closely associated element, arsenic.

## I. HARRIS METHOD

The sample is prepared by the digestion procedure used in the official<sup>7</sup> and bromate<sup>8</sup> methods for the determination of arsenic. After preliminary separation as the sulfate, lead is converted to the chromate and the chromate ion is determined iodometrically. The method follows:

## REAGENTS

- \*(1) *Nitric acid*.—Concentrated. Approximately 67% of  $\text{HNO}_3$ .
- \*(2) *Sulfuric acid*.—Concentrated. Approximately 93% of  $\text{H}_2\text{SO}_4$ . Dilution: 1 + 19 (approximately 8% by weight).
- \*(3) *Ammonium oxalate solution*.—Saturated.
- \*(4) *Ammonium acetate solution*.—40%, W/V. Dissolve 40 grams of  $\text{NH}_4\text{C}_2\text{H}_3\text{O}_2$  in water, add 2 cc. of 0.1 N  $\text{H}_2\text{SO}_4$ , dilute to 100 cc., and filter.
- (5) *Potassium chromate solution*.—5%, W/V. Dissolve 5 grams of  $\text{K}_2\text{CrO}_4$  in water, dilute to 100 cc., and filter.
- (6) *Potassium iodide solution*.—15%, W/V. Dissolve 15 grams of the purest KI in  $\text{CO}_2$ -free water and dilute to 100 cc. Prepare as frequently as is necessary to prevent formation of sufficient free iodine to produce the starch iodide color when mixed with the reagents used in the titration. (The solu-

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<sup>4</sup> U. S. Food and Drug Adm., Washington, D. C.

<sup>5</sup> U. S. Food and Drug Adm., New York, N. Y.

<sup>6</sup> U. S. Food and Drug Adm., Washington, D. C.

<sup>7</sup> *Methods of Analysis*, A. O. A. C., 308 (1930).

<sup>8</sup> *This Journal*, 16, 75 (1933).

tion may be rendered very slightly alkaline with one or two drops of 0.1 *N* NaOH to retard formation of free iodine.)

- (7) *Standard sodium thiosulfate solution*.—0.1 *N*. Dissolve 24.83 grams of  $\text{Na}_2\text{S}_2\text{O}_3 \cdot 5\text{H}_2\text{O}$  in 1 liter of  $\text{CO}_2$ -free distilled water. Protect the solution with a soda lime tube and a thiosulfate trap and allow it to stand, preferably for about two weeks, before standardizing. Standardize once a month against resublimed iodine, potassium iodate or bi-iodate, or standard  $\text{K}_2\text{Cr}_2\text{O}_7$  solution. Prepare a fresh 0.01 *N* or 0.005 *N* solution at least semi-weekly by diluting the 0.1 *N* solution with  $\text{CO}_2$ -free distilled water.

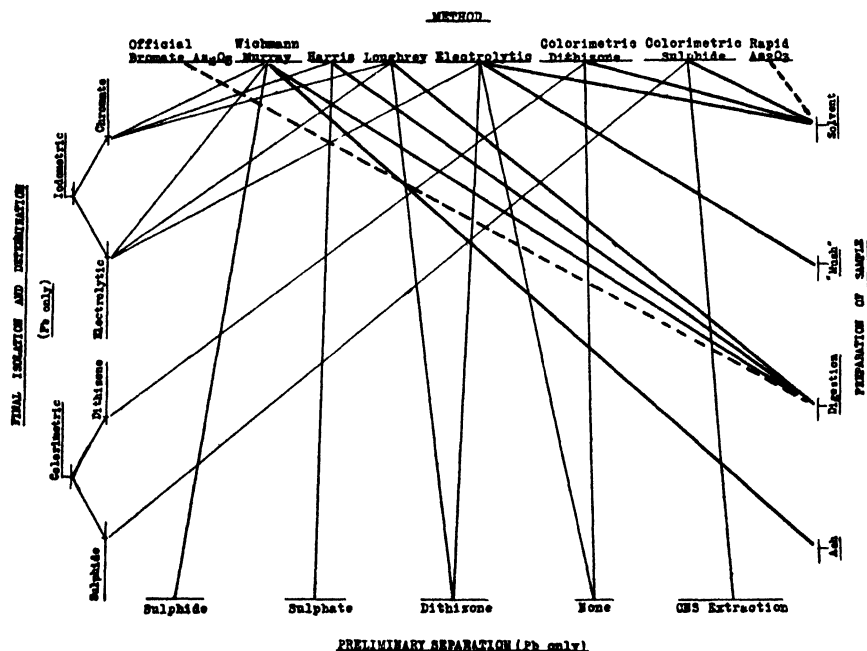


FIG. 1. CORRELATION OF METHODS FOR DETERMINATION OF LEAD AND ARSENIC

- (8) *Starch solution*.—Mix 1 gram of potato starch, or preferably soluble starch, with water to form a thin paste; add to 200 cc. of boiling water and continue boiling 1 minute. Prepare a fresh solution at least weekly.

\*(9) *Ethyl alcohol*.—95% by volume.

\*(10) *Glacial acetic acid*.

\*(11) *Hydrochloric acid*.—Approximately 35% of HCl. Dilution 1 + 4.

NOTE:—Reagents marked (\*) should be as free from lead and arsenic as it is possible to obtain them. Reagents marked (+) may attack soft glass and therefore should be kept in Pyrex or similar hard glass. Lead contamination from glassware should be prevented by using Pyrex or similar hard glass of minimum lead content for all determinations and by rinsing all containers first with hot 40 per cent ammonium acetate solution and then with hot distilled water.

As it is impracticable to obtain absolutely lead-free reagents, a blank determination should be conducted on each new lot of reagents in the quantities used in the method and the result corrected accordingly.

## PROCEDURE

*Preparation of Sample.*—Digest the sample (in an amount to contain 1 mg. or more of Pb) as directed under 3, p. 307, *Methods of Analysis*, A.O.A.C., 1930. If digestion can be made in large beakers, the following procedure is convenient: Dry the sample overnight in an oven or on a hot plate or steam bath at approximately 100°C. Wet the material with 100 cc. of  $\text{HNO}_3$ , cover with a watch-glass, and allow to stand until excessive frothing subsides. Heat cautiously on a hot plate or over a free flame at a temperature of 130°–140°C. until copious evolution of nitric oxide fumes ceases, remove, and add slowly 20 cc. of  $\text{H}_2\text{SO}_4$ . Replace on the hot plate and heat carefully until frothing subsides, then boil until the mixture turns brown. Proceed as directed in the reference given above for the production of a water-white residue, free from all oxides of nitrogen.

Allow the residue to cool, add to the Kjeldahl flask or beaker 40 cc. of water, and transfer to a 400 cc. beaker. Wash out the container with 40, 20, 20, 10 and 10 cc. portions of water, draining thoroughly after each washing. (It is essential to reduce sulfuric acid from the container to less than the equivalent of 1 cc. of 0.1 N  $\text{H}_2\text{SO}_4$ , as an excess may unduly increase the concentration of sulfuric acid in succeeding reagents.) Add 15 cc. of the hot 40% ammonium acetate reagent (4) to the container to dissolve any residual  $\text{PbSO}_4$ . (Any silica present will remain undissolved.) Reserve the washings and use for the first extraction under "Isolation." Add to the diluted digested material slowly, while stirring, 125 cc. of alcohol to precipitate the lead (some other sulfates will also precipitate), so regulating the rate as to assure that the entire amount is added uniformly during a period of about 2 minutes. Cover, and allow to stand overnight.

*Isolation.*—Decant through a 12.5 cm. filter (C.S. & S. Blue Ribbon No. 589 or equivalent), retaining as much as possible of the precipitate in the beaker, and allow the filter to drain. Place the beaker containing the bulk of the precipitate on a water bath and evaporate the remaining alcohol until the precipitate appears just damp. (Do not allow the precipitate to dry sufficiently to cake.) Wash down the walls of the beaker with 20 cc. of  $\text{H}_2\text{SO}_4$  (1+19) and stir. Remove as much of the precipitate as possible to the filter and allow to drain thoroughly. Wash out the beaker with 10 cc. portions of 50% alcohol, draining the filter thoroughly each time; remove all adhering precipitate from the beaker walls to the filter; and finally wash the entire mass on the filter with 95% alcohol until the washings are free from mineral acid (test with moist litmus paper).

After evaporation of the alcohol, the filtrate may be used for the determination of arsenic.

Expel alcohol from the precipitate by drying in an oven at 100°C. Carefully remove the filter paper from the funnel and unfold it over a 150 cc. beaker, thus transferring the major portion of the precipitate to the beaker. Replace the filter in the funnel. Add the ammonium acetate solution reserved under "Preparation," to the precipitate in the beaker, cover with a watch-glass, and cautiously bring to a boil. Allow to settle and decant as much of the liquid as possible through the same filter paper, collecting the filtrate in a 400 cc. beaker. Repeat the process with another 15 cc. portion of the hot ammonium acetate, (4), then with three portions of 10 cc. each of the same reagent. (The total volume of ammonium acetate solution must be carefully restricted to 60 cc.) During the process thoroughly wash all portions of the filter paper with the hot ammonium acetate solution. Transfer the residual precipitate to the filter and wash with about 150 cc. of cold water from a wash bottle.

[Extraction of the mixed sulfates with ammonium acetate containing sulfuric

acid separates lead from barium<sup>1</sup> (occurring principally as the residue of barium-containing insecticides) by depressing the solubility of the barium. Sulfuric acid, in excess of 8 cc. 0.1 *N* H<sub>2</sub>SO<sub>4</sub> per 100 cc. of reagent will depress the solubility of PbSO<sub>4</sub> (especially in the presence of calcium and alkali sulfates) as well as that of BaSO<sub>4</sub>. Therefore a minimum is desirable, but an excess derived from all sources must be avoided. Unless removed, barium will be precipitated later, together with lead, as the chromate, and thus cause high results.]

Add 3 cc. of glacial acetic acid to the filtrate, stir the mixture thoroughly, bring to room temperature and while stirring add 20 cc. of the potassium chromate (5). Stir for 2 minutes after the precipitate of lead chromate appears. (A precipitate of PbCrO<sub>4</sub> equivalent to less than 1 mg. of lead may not be visible.) Cover, heat to boiling, boil gently for 10 minutes, and allow to stand overnight. (As lead chromate precipitates slowly from strong hot acetate solutions, standing overnight is imperative for accurate results. The amount of acetate for extraction must be limited and the final concentration must be brought below 24 grams per 100 cc. to prevent the precipitation of a double chromate of lead and ammonium.)<sup>2</sup>

Decant as thoroughly as possible through a moistened 11 cm. filter paper (C.S. & S. Blue Ribbon No. 589 or equivalent), wash, filter repeatedly with small portions of hot water, transfer the precipitate to the filter, and wash beaker and filter with hot water until all traces of soluble chromate are removed. Use special care to assure that air pockets between paper and funnel retain no soluble chromate. Remove with a policeman all traces of precipitate adhering to the sides of the beaker. Continue the washing until 10 cc. of the filtrate remains colorless and clear on addition of a few drops of a neutral 10% solution of silver nitrate.

*Determination.*—Dissolve the lead chromate on the paper with 6 cc. or more of HCl (1+4), receiving the filtrate in a glass-stoppered Erlenmeyer flask. Allow the acid to permeate all portions of the filter. Wash with cold water until the total volume of the filtrate approximates 12 times the volume of acid used. Add 3 cc. of the potassium iodide (6), stopper the flask immediately, and allow to stand 5 minutes. Titrate with the 0.01 *N* thiosulfate solution (7), using starch as an indicator toward the end of the titration. 1 cc. of 0.01 *N* thiosulfate is equivalent to 0.690 mg. of Pb.

## DISCUSSION

Method I is applicable to all food samples that may be digested in a quantity sufficient to yield 1 mg. or more of lead. Alcohol precipitates very impure lead sulfate in the presence of iron (over 75 mg.), calcium and alkali sulfates, or silica. Under these conditions iron as well as other interfering elements may not be entirely removed in the sulfate separation. If they are carried through to the lead chromate precipitation, they will cause serious interference and erratic results. With this exception, the method has given satisfactory results in the hands of analysts experienced in the procedure. Recoveries of lead added to lead-free apple peelings, together with a liberal dose of such contaminants as might be found on sprayed fruits or vegetables, have been 95 per cent or better. The most serious criticism of the method is the time required (about 3 days). No new principles are involved, but those used had not been previously applied to the analysis of spray residue on fruits and vegetables.

<sup>1</sup> Scott, *Standard Methods of Chemical Analysis*, 1917 Ed., p. 235.

<sup>2</sup> Unpublished data from E. O. Haenni, U. S. Food and Drug. Adm., Cincinnati, O.

## II. WICHMANN-MURRAY METHOD

After determining arsenic on the sample by the bromate method (modified to substitute hydrazine as the reducing agent)<sup>1</sup> the residue is used for the estimation of lead by a modified Fairhall<sup>2</sup> procedure. The original Fairhall method separates the lead by repeated precipitation as sulfide, converts the lead sulfide to the chromate, and determines the chromate ion iodometrically. The principal modification is the control of the pH of the sulfide and chromate isolations (1) to avoid the co-precipitation of elements that commonly interfere, (2) to eliminate the necessity for more than one sulfide precipitation, and (3) to reduce the difficulty of obtaining a satisfactory chromate precipitate.

## NEW REAGENTS

- \*(12) *Sodium bromide-hydrazine sulfate reducing solution*.—Dissolve 20 grams of  $\text{N}_2\text{H}_4 \cdot \text{H}_2\text{SO}_4$  and 20 grams of  $\text{NaBr}$  in 1 liter of  $\text{HCl}$  (1+4).
- \*(13) *Ammonium acetate*.—20% W/V. Dissolve 20 grams of  $\text{NH}_4\text{C}_2\text{H}_3\text{O}_2$  in water, add 2 cc. of 0.1 N  $\text{H}_2\text{SO}_4$ , and dilute to 100 cc.
- (14) *Indicators*.—0.04% solutions: bromocresol green, bromphenol blue, and thymol blue.
- \*(15) *Citric acid*.—C.P.
- \*(16) *Ammonium hydroxide*.—Approximately 28%  $\text{NH}_3$ .
- +\*(17) *Sodium hydroxide solution*.—10% W/V. Dissolve 100 grams of  $\text{NaOH}$  in water and dilute to 1 liter. If a precipitate appears at any time, filter through acid-washed asbestos.
- \*(18) *Formic acid*.—C.P.
- +\*(19) *Sodium hydroxide-sulfide*.—Dissolve 480 grams of  $\text{Na}_2\text{S} \cdot 9\text{H}_2\text{O}$  and 40 grams of  $\text{NaOH}$  in water, add 16 grams of powdered sulfur, shake until the sulfur dissolves, filter, and dilute to 1 liter.
- \*(20) *Sodium bromate or sodium chlorate*.—C.P.
- (21) *Potassium bichromate solution*.—5% W/V. Dissolve 5 grams of  $\text{K}_2\text{Cr}_2\text{O}_7$  in 100 cc. of water and filter.

## PROCEDURE

*Preparation of Sample and Determination of Arsenic*.—Proceed as directed in the bromate method,<sup>3</sup> with the following exception: substitute 25 cc. of the hydrazine sulfate reagent (12) for the "0.5 gram  $\text{KBr}$  (or  $\text{NaBr}$ ), 2 grams  $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ " mixture specified (p. 76, l. 3, par. 3, under "Procedure"). Use a sample containing at least 1 mg. of  $\text{Pb}$ . (The residue in the Kjeldahl flask at the end of the distillation should not be less than 50–60 cc.; otherwise there will be distilled  $\text{SO}_2$ , which will titrate with the bromate as arsenic.)

*Isolation of Lead*.—Disconnect<sup>4</sup> the distilling tube from the Kjeldahl flask, add about 100 cc. of distilled water, and filter with suction on a fritted glass filter. (Fritted Jena glass filter No. 11G4 or equivalent, Büchner type. Diam. of disc 40 mm., height above disc 50 mm., diam. of tube 1–8 mm., capacity 60 cc.) Collect the filtrate in a 500 cc. glass-stoppered Erlenmeyer flask with the help of a bell jar, and use the same flask throughout the procedure. At this point thoroughly wash with hot water, the silica, barium sulfate, calcium sulfate and any other insoluble

<sup>1</sup> *This Journal*, 16, 75, 325 (1933).

<sup>2</sup> *J. Ind. Hygiene*, 4, 9 (1922); Public Health Bull. 163 "The Use of Tetraethyl Lead Gasoline in Its Relation to Public Health."

<sup>3</sup> *This Journal*, 16, 75 (1933).

materials on the fritted glass filter, and also pulverize any large granules of precipitate with the flattened end of a stirring rod. Bring into solution any lead sulfate in the Kjeldahl flask by means of 10 cc. of the hot ammonium acetate (13), pour this liquid over the residue on the filter, and thoroughly rinse both flask and filter with hot water. (The filtrate is sometimes slightly cloudy following this extraction, due largely no doubt to traces of silica or barium sulfate. However, silica has no influence on the final result, and the effect of the barium in the quantity involved has been found to be negligible. The filtrate should now have a volume of from 200 cc. to 350 cc.) Add 5 grams of citric acid and 10 drops of thymol blue indicator. Cool and add ammonia from a buret slowly and with constant agitation while the color of the solution changes from red through orange to a distinct yellow ( $pH$  2.8), which is the end of the acid range of thymol blue indicator. To fix the  $pH$  more accurately, add 3 or 4 drops of bromphenol blue.

(The color changes of bromphenol blue range from yellow at  $pH$  3.0 through olive or dirty green to a purple at 3.4 or above. The  $pH$  range for the quantitative precipitation of lead sulfide without co-precipitation of iron sulfide is from 2.5–3.4,<sup>1</sup> or from orange-yellow with thymol blue to incipient purple or olive-green with bromphenol blue.) Make adjustment to the optimum  $pH$  *only from the acid side*, thus avoiding any permanent precipitation of phosphates or hydroxides. (Addition of citric acid, cooling of the solution, and agitation should prevent the precipitation of aluminum, ferric or alkaline earth phosphates or hydroxides, which would interfere later in the lead chromate precipitation.) If the solution, after severe shaking, is still cloudy, add sufficient  $HCl$  to clear it; then add a few grams of citric acid, cool, and repeat the adjustment of  $pH$  more carefully. When enough iron is present to mask the color, make the final adjustment of  $pH$  with the help of a spot plate. (With less than 1 mg. of lead the precipitation of lead sulfide may proceed slowly at  $pH$  2.5–3.0, and the precipitate may not coagulate readily. Copper (5–10 mg.) acts as a good collector of lead; if none is present, it may be added.) When iron is low the  $pH$  range 3.0–3.2 is preferred (olive or dirty green bromphenol blue), but if there is sufficient iron to color the solution strongly, especially when lead and copper are present in appreciable quantity, keep the  $pH$  of the solution lower (2.8–3.0, yellow with either one or both indicators), otherwise the sulfide may be contaminated with a little iron, which would interfere later. (When the optimum  $pH$  for the particular sample is reached, the solution should be clear.)

Now pass a rapid current of hydrogen sulfide through the solution until it is thoroughly saturated (2 or 3 minutes should be sufficient), and filter the sulfides immediately on a second fritted-glass filter of the type previously used. (If only one filter is available, thoroughly clean it between filtrations with concentrated  $H_2SO_4$ , strong  $HCl$ , or 10%  $NaOH$ , followed immediately by a reverse flushing with hot water. Glass filters vary in rapidity of filtration. A very light mat of asbestos may be used, therefore, to prevent flocculent precipitates from clogging the filter or to close any unusually large pores.) If the sample is suspected to contain tin or antimony, or the arsenic distillation has been omitted, dissolve the tin, arsenic, or antimony sulfides from the flask and filter with three to six applications of about 5 cc. each of warm sodium hydroxide-sulfide (19). (Copper sulfide is partially soluble in this reagent and may reprecipitate in the filtrate, but a thin mat of asbestos placed on the glass filter will usually prevent peptization and loss of lead sulfide.) Wash the flask and sulfides three or four times with small portions of  $H_2S$  water adjusted to  $pH$  3.0. Place the Erlenmeyer flask in which the "sulfiding" was done in the bell jar in order to receive the dissolved sulfides and thus obviate "policing" this container.

<sup>1</sup> Patten and Mains, *This Journal*, 4, 233 (1920).



Disconnect the suction, add to the precipitate of sulfides 3 or 4 cc. of  $\text{HCl}$  (1+1) and a few crystals of either  $\text{NaBrO}_3$  or  $\text{NaClO}_3$ , and quickly cover the filter with watch-glass. (The reaction proceeds with reasonable rapidity, and the sulfides are completely dissolved in 4 to 6 minutes.) If complete solution does not result, add a few more crystals of oxidizing reagents. (Any clean elementary sulfur remaining on the fritted glass in no way affects the determination.) Apply suction, rinse the watch-glass, and wash down the walls of the filter thoroughly with hot water. Remove the flask from the bell jar, add one or two small glass beads to prevent bumping, and heat the solution to boiling. (The free halogen should oxidize any colloidal sulfur that may be present in the solution. If it is insufficient, add a further *small* portion of sodium bromate.) Continue boiling until the free halogen is practically expelled and add a few drops of formic acid to complete its removal. Adjust the volume to approximately 100 cc. Bring the  $\text{pH}$  of the solution to 4.5–5.0 (blue-green) *from the acid side* with 10%  $\text{NaOH}$  solution, using bromocresol green as indicator. Heat to boiling and allow to stand 5–10 minutes. (The solution should be clear and green to blue-green in color.)

(The method is designed to assure the isolation of lead from interfering elements in the sulfide or in subsequent chromate precipitations. The principal interferences that are likely to be present are ferric iron, aluminum, tin, barium, phosphates or arsenates. Iron, aluminum or tin hydroxides or phosphates are insoluble at the  $\text{pH}$  range of 4.5–5.0. They will occlude lead, and ferric chloride may in addition liberate iodine from potassium iodide under some conditions. Lead phosphate or arsenate is also insoluble. Bismuth, copper, cadmium, mercury or zinc sulfides are insoluble at  $\text{pH}$  3.0, but they do not form insoluble hydroxides or chromates at  $\text{pH}$  4.5–5.0. Mercurous mercury will be oxidized in the digestion. Bismuth and antimony may prove troublesome on account of formation of oxychlorides, but fortunately they are seldom present in spray residues.)

If a precipitate forms, indicating incomplete removal of one or more of the above interferences, add  $\text{HCl}$  and about 1 gram of citric acid, adjust to  $\text{pH}$  2.8–3.0 with ammonia, and repeat the precipitation of the sulfides. If the solution remains clear, heat to boiling, and add 5 cc. of  $\text{K}_2\text{Cr}_2\text{O}_7$  (21) slowly by means of a pipet. Boil gently or digest on a steam bath for 15–30 minutes, or until the precipitate coagulates. Cool, and allow to stand from 2 to 4 hours. If the quantity of lead is less than 1 mg., allow the precipitate to stand at least 4 hours, preferably overnight. (If the precipitate coagulates well and the supernatant liquid is clear, 2 hours is sufficient. Interference of ammonia compounds with the precipitation of lead chromate in this method is negligible.)

Proceed as directed in Method I, beginning "Decant as thoroughly as possible . . ." Unless the quantity of lead is very small (less than 1 mg.), use the fritted-glass filter for filtration of the chromate to facilitate removal of the soluble chromate, but wash the sides of the filter well to clean any "creeping" lead chromate. If 0.005  $N$  thiosulfate is substituted for the 0.01  $N$  solution in the titration, 1 cc. is equivalent to 0.345 mg. of Pb.

## RESULTS WITH METHOD II

To test the reliability of this method in the presence of such interferences as might normally be expected in spray residues, several portions of lead-free apple peelings were digested with known quantities of lead and the following interferences: 5 mg. Mn, 25 mg.  $\text{P}_2\text{O}_5$ , 15 mg. Fe, 100 mg.  $\text{CaSO}_4$ , 5 mg. Ba, 5 mg. Al, 10 mg. Cu, and 20 mg.  $\text{SiO}_2$ . The results in Table 1, obtained by Murray, indicate the reliability of the method. The amount of lead added was unknown to the analyst.

TABLE 1

*Recovery of lead from lead-free apple peelings*

Pb PRESENT mg.	Pb DETERMINED mg.
.73	.72
1.37	1.35
.92	.95
1.86	1.90
.58	.49

## II A AND B. ALTERNATIVE PROCEDURES FOR PREPARATION OF SAMPLE FOR WICHMANN-MURRAY METHOD

## NEW REAGENTS

- \*(22) *Hydrobromic acid-bromine mixture*.—To 500 cc. of 35%, or stronger, HBr, add 70 cc. of liquid bromine.
- \*(23) *Hydrochloric-citric acid solution*.—Dissolve 50 grams of citric acid in 250 cc. of HCl (1+4).

A.—Some samples may be more conveniently ashed than digested. Arsenic may be largely lost on ashing, but if the temperature does not exceed 550°C.,<sup>1</sup> no lead is volatilized. Ashing has been found satisfactory on dry pectin, dried apples, and tea, and probably will be satisfactory and convenient for many other similar substances, and also for biological material. The procedure follows:

Weigh into a porcelain casserole or silica dish sufficient sample to yield at least 1 mg. of Pb. If not dry, desiccate the sample in an oven at 130°C., preferably overnight. Place the casserole in a cold muffle and allow the temperature to rise gradually to 350°C. When most of the volatile matter has been driven off, raise the temperature to 500°C., taking care that the heat of combustion of the carbonaceous matter does not bring the temperature higher than 500°C. Or, if a muffle furnace with a temperature control is available, allow the ashing to proceed overnight with the control set at 350°C., in which case 1 hour's heating at 500°C. next morning is generally sufficient to secure a good ash.

Cool, cover the casserole with a watch-glass, and through the lip of the dish add sufficient strong HCl to dissolve the ash. Rinse the watch-glass with water and evaporate the sample to dryness on a steam bath. Then add 5–10 cc. of the HBr–Br reagent (22) and again evaporate on the steam bath. (This procedure will volatilize tin<sup>2</sup> as well as arsenic, but not antimony or bismuth. In the absence of arsenic or tin these last two steps may of course be omitted.) Take up the ash in 50 cc. of HCl (1+1) and heat to boiling. Filter, and wash the residue with hot water, collecting the filtrate and washings in a 500 cc. glass-stoppered Erlenmeyer flask. A small quantity of carbon in the residue is permissible, but if a large amount is present, return the filter and residue to the casserole, dry, and reash. Rinse the casserole and extract the residue (or reashed residue) with 50 cc. of the hot HCl-citric acid reagent (23), collecting the clear extract in the glass-stoppered Erlenmeyer. Then rinse the casserole and extract the residue with 20 cc. of hot 40% ammonium acetate (4). Wash casserole and residue thoroughly with hot water. (These extractions should bring refractory lead compounds into solution.<sup>3</sup>) Cool the filtrate, add 1 cc. of thymol blue indicator, and proceed as directed under "Isolation" Method II, beginning "add ammonia from a buret. . ."

<sup>1</sup> Fairhall, *Loc. cit.*

<sup>2</sup> H. Fischer, *Wiss. Veröffentlich. Siemens Konzern*, 12, 44 (1933).

<sup>3</sup> *J. Ind. Hygiene*, 4, 19 (1922); Public Health Bull. 163.

In Table 2 are given data obtained by Vorhes and Clifford on the recovery of lead added to lead-free apple sauce. The lead was recovered by the ashing procedure but actually determined by an electrolytic method to be described later.

TABLE 2  
*Recovery of lead from 200 grams of lead-free apple sauce*

Pb ADDED mg.	Pb RECOVERED mg.
0.10	0.11
0.30	0.30
0.50	0.48
1.00	0.97
2.00	1.87

B.—Sodium and calcium phosphates have been handled successfully by this method by using the following procedure for preparation of sample:

In a 400 cc. beaker dissolve 50 grams of the sample in the smallest practicable volume of solution by warming and alternately adding small quantities of water and HCl. (In commercial phosphates a small insoluble residue usually remains.) Filter into a 500-cc. glass-stoppered Erlenmeyer flask. (A clear filtrate must be obtained. A fritted-glass filter is useful for this purpose.) Rinse the beaker and extract the residue on the filter with 20 cc. of hot HCl-citric acid reagent (23). Rinse with hot water and extract with 20 cc. of hot 40% ammonium acetate (4). Finally rinse beaker and filter with hot water, add 5 grams of citric acid to the filtrate, cool, and proceed as directed under "Isolation," Method II, beginning "add ammonia from a buret . . . ."

With calcium phosphate samples, the adjustment of the solution to pH 3.0 before sulfiding is troublesome. The heavy precipitate caused by the local action of the ammonia, if not formed in too large quantities, may usually be redissolved by shaking. If the solution is kept cold, sufficient citric acid is present, and the ammonia added slowly with vigorous agitation, the precipitate should redissolve at a pH less than 2.8–3.0. If it is impossible to redissolve the precipitate by violent shaking, add sufficient HCl to clear the solution, cool, add more citric acid, and approach the proper pH more carefully. Alkaline earth phosphates or citrates will precipitate after a few hours' standing at pH 3.0.<sup>1</sup> For this reason, no extended period of time should elapse between adjustment to the desired pH and filtration of the sulfides. The volume of the solution should approximate 350–400 cc. when adjustment of pH is obtained.

## DISCUSSION

Methods II, IIA, and IIB are generally applicable to food products in samples of such size as to yield 1 mg. or more of Pb. An electrolytic separation and iodometric titration of the PbO<sub>2</sub> (described later) may be substituted for the chromate estimation given, in which case analyses on samples containing as low as 0.25 mg. of lead, or even 0.05 in special cases, may be made with reasonable accuracy.

The character of the results obtained by Vorhes on lead-free phosphates is indicated by Table 3. Calcium phosphate was made from calcium

<sup>1</sup> *Loc. cit.*

chloride and sodium hydrogen phosphate especially purified from lead. Known quantities of lead were added to and recovered from 50 grams of this material as described above and determined by the lead chromate process.

TABLE 3

*Recovery of lead from calcium phosphates by chromate method*

LEAD ADDED mg.	LEAD RECOVERED mg.
1.00	0.96
2.00	1.87
5.00	4.92
10.00	9.88

### III. LOUGHREY'S METHOD

This method utilizes the remarkable affinity of diphenylthiocarbazone ("dithizone") in chloroform solution for lead in separating the lead from common interferences, according to H. Fischer and others.<sup>1</sup> The organic lead compound is then decomposed, and lead is precipitated as the chromate and determined indirectly by iodometric titration of the chromate ion.

#### NEW REAGENTS

- \*(24) *Citric acid solution*.—20% W/V. Dissolve 50 grams of citric acid in water and dilute to 250 cc.
- \*(25) *Potassium cyanide solution*.—10% W/V. Dissolve 25 grams of KCN in water and dilute to 250 cc.
- \*(26) *"Dithizone"*.—0.05%, 0.025% and 0.01% W/V solutions in chloroform. As diphenylthiocarbazone ("dithizone") prepared commercially is seldom pure, purify it as follows: Dissolve 1 gram in 50 cc. of chloroform and shake out in a separatory funnel with 3–100 cc. portions of dilute ammonia (1+99). Reserve the chloroform solution for further recovery of dithizone. (The impurity of successive ammoniacal extractions will be increasingly evident, but the first three extractions will generally be satisfactory.) Combine the ammoniacal extracts in a large separatory funnel and acidify slightly with dilute hydrochloric acid. Dissolve out the precipitated dithizone with two or three 20 cc. portions of chloroform. Combine the chloroform extracts in a separatory funnel and wash two or three times with water. Evaporate the chloroform with *gentle* heat on a steam bath. It is best to remove the last traces of chloroform at a temperature of not more than 50°C. in vacuo. The reagent solutions are made up to contain 50 mg., 25 mg., and 10 mg., respectively, of the dry purified dithizone per 100 cc. of chloroform.
- (27) *Dilute ammonia*.—(1+99).
- (28) *Chloroform*.—U.S.P.

<sup>1</sup> E. Fischer, *Ann.*, 190, 67 (1878); 212, 316 (1882); H. Fischer, *Z. angew. Chem.* 42, 1025 (1929); *Wiss. Veröff. Siemens Konzern*, 12, 44 (1933); C. A. 27, 3418 (1933); Allport and Shrimshire, *Analyst*, 57, 440 (1932).

## PROCEDURE

*Preparation of Sample.*—Digest the sample (in an amount to contain 1 mg. or more of Pb.) as directed under 3, p. 307, *Methods of Analysis, A.O.A.C.*, 1930.

*Isolation.*—Dilute the digested residue in the Kjeldahl flask with 50–100 cc. of water, cool, and add 15 cc. of 20% citric acid. Neutralize to litmus with strong ammonia and add 1–2 cc. in excess. Transfer to a 500 cc. short-stemmed separatory funnel, rinsing the Kjeldahl thoroughly (volume of solution 150–250 cc.). Add 5 cc. of 10% KCN (in the presence of ferric iron this quantity must be reduced, because excess KCN and iron will oxidize the dithizone), and 15 cc. of 0.05% dithizone reagent. Stopper the funnel and shake vigorously, releasing the pressure by inverting and opening the stopcock. (Lead forms a cherry-red chloroform-soluble compound with dithizone. This color may be modified by excess of the green dithizone.) Allow the chloroform layer to separate and draw it off into a 125 cc. short-stemmed separatory funnel containing 20 cc. of dilute ammonia (27). Follow the progress of the extraction by observation of the color of the chloroform layer, because the color of the first extract governs the strength of the dithizone solutions used for subsequent extractions. Re-extract with the stronger reagents until the purple shade is obtained and thereafter with the 0.01% reagent until two successive extractions show the negative green. (One extraction with the 0.05% reagent, together with three or four extractions with the weaker ones, are generally sufficient for ordinary quantities of lead, but with large quantities it is advisable to make more extractions with the stronger solution. Even 0.1% dithizone solution may be necessary in some cases. Oxidizing agents should be absent as they will oxidize the dithizone readily to yellow compounds soluble in chloroform.) Shake the smaller funnel, allow the layers to separate, and draw off the lower layer into a 150 cc. beaker, making as clean a separation as possible. Swirl the funnels to loosen any chloroform solution which may adhere to the sides. Evaporate the chloroform from the beaker on a steam bath. As the last traces of chloroform in the funnels will have separated by this time, draw these off through the smaller funnel into the beaker and evaporate to dryness.

Add a few cc. of  $\text{HNO}_3$  (1+1), and a few crystals of  $\text{KClO}_3$ , and warm gently until the organic material is destroyed. Evaporate to dryness on a steam bath. Take up the residue in a few cc. of dilute  $\text{HCl}$  (1+4) and dilute to about 50 cc. Adjust the pH to 4.5–5.0 (blue-green) with 10%  $\text{NaOH}$ , using bromocresol green. Proceed as directed in Method II, beginning “. . . heat to boiling and add 5 cc. of 5%  $\text{K}_2\text{Cr}_2\text{O}_7$  solution. . . .”

## DISCUSSION

The presence of barium sulfate or of a large quantity of calcium sulfate causes low results owing to the occlusion of lead in these substances and consequent interference in the dithizone extraction. Tin and bismuth are extracted by the dithizone along with the lead and interfere in the chromate precipitation. Other elements that commonly interfere in the chromating are eliminated by the dithizone extraction. Electrolytic separation of  $\text{PbO}_2$  after partial destruction of the dithizone compound with  $\text{HNO}_3$ , as hereinafter described, may be practiced to advantage especially in cases where the lead is less than 1 mg.

The method (with lead chromate precipitation) has been successfully applied to samples that could be digested in sufficient amounts to give a quantity of lead greater than 1 mg., and that did not introduce interferences of tin, barium, and calcium sulfate.

## IV. COLORIMETRIC SULFIDE METHOD (WICHMANN-VORHES)

This method is primarily designed for rapid approximate determinations of lead on fresh apples and pears. Spray residue is removed from the fruit by means of solvents; the solution is freed from organic coloring matter and common interferences (the most important of which is iron); and lead is estimated colorimetrically as the sulfide.<sup>1</sup>

Solvents have long been used in control laboratories for rapid preparation of fresh apple and pear samples for approximate estimation of arsenic by the Gutzeit method. The Association of Official Agricultural Chemists has given no official recognition to this method of preparation, however, because incomplete removal of the spray residue by solvents is a recognized fact. The solvent treatment used in the past for arsenic determinations consisted of immersion of the fruit in hot alkali followed by rinsing with hot water.

This method combines an alkaline immersion with an acid rinse and introduces a detergent in the alkali. The efficiency of this treatment in removal of lead or arsenic will approximate 95 per cent or better with even the most refractory fruit. The method follows:

## NEW REAGENTS

- +\*(29) *Sodium hydroxide solution*.—30% W/V. Dissolve 300 grams of NaOH in water and dilute to 1 liter. If a precipitate appears at any time, filter through acid-washed asbestos.
- +\*(30) *Sodium oleate*.—10% W/V. To 45 cc. of 30% NaOH and 400 cc. of water in a 1.5 liter beaker, slowly add 90 grams of oleic acid while heating and stirring. When all the acid has been added, dilute slowly to about 900 cc., continuing the heating and stirring. Avoid vigorous boiling and consequent excessive foaming. Heat the mixture on a steam bath until the soap is entirely dissolved. (A small flocculent precipitate of impurities may remain.) Cool, dilute to 1 liter, mix, and filter.
- \*(31) *Nitric acid*.—(1+49) and (1+4).
- \*(32) *Bromine water*.—Saturated.
- \*(33) *Hydrogen peroxide*.—30%. Keep cool to prevent rapid deterioration.
- \*(34) *Urea solution*.—30% W/V. Dissolve 30 grams of urea in water and dilute to 100 cc. Filter if not perfectly clear.
- \*(35) *Ammonium sulfocyanide solution*.—Prepare a saturated solution (at room temperature) of  $\text{NH}_4\text{CNS}$  in water. To prevent any precipitation upon change of room temperature, add 5 cc. of water in addition for each 100 cc. of solution. Add a few drops of  $\text{HNO}_3$  (1+4). Allow the mixture to stand overnight (to oxidize any ferrous iron), and if more than a very slight pink color develops extract with amyl alcohol in a separatory funnel. (Several extractions may be necessary to remove the color.) Filter on an acid-washed filter (Whatman No. 41 or equivalent). Reserve the amyl alcohol for recovery.
- \*(36)  *$\text{HNO}_3$ - $\text{NH}_4\text{CNS}$  solution*.—Dilute 2 cc. of reagent (35) to 90 cc. and add 10 cc. of  $\text{HNO}_3$  (1+4). Prepare fresh daily.
- (37) *Amyl alcohol*.—B.P. 128°–132°C. Reserve used amyl alcohol and recover

<sup>1</sup> Hamenoc, *Analyst*, 57, 622 (1932).

as follows: Wash twice with water in a separatory funnel. Render alkaline with dilute ammonia and wash with water three times. Make acid with dilute  $\text{HNO}_3$ . The red color of ferric thiocyanate should be absent; if it is not, make alkaline again with ammonia and wash with water until the red color does not reappear upon acidification. Wash the acidified alcohol free from acid and filter.

- \***(38)** *Gum acacia solution*.—0.5% W/V. Wet 0.5 gram of light-colored U.S.P. powdered gum acacia with a minimum (about 2 cc.) of 95% alcohol and add rapidly 100 cc. of water, mixing with a swirling motion. Filter through an acid-washed filter (Whatman No. 41 or equivalent). Prepare fresh daily.
- +**(39)** *Sodium sulfide solution*.—1% W/V. Wash about 12 grams of large crystals of  $\text{Na}_2\text{S} \cdot 9\text{H}_2\text{O}$  with a minimum of cold water. Discard the washings, dissolve the crystals (about 10 grams) in water, and dilute to 1 liter. Filter through acid-washed asbestos if not perfectly clear.
- +**(40)** *Sodium sulfide-gum solution*.—Mix 10 volumes of reagent (39) with one volume of reagent (38). Prepare fresh daily.
- +**(41)** *Ammonia-potassium cyanide-citrate solution*.—Dilute one volume of concentrated ammonia with three volumes of water and add 2% W/V. KCN and 3% W/V citric acid. Filter, if necessary, through acid-washed asbestos and preserve in some form of dispensing apparatus.
- (42)** *Standard lead solution*.—Lead nitrate may be recrystallized from water to obtain a product of great purity. Dissolve 20–50 grams of C.P. lead nitrate in a minimum of hot water and cool with stirring. Filter the crystals with suction on a small Büchner funnel, redissolve, and repeat the crystallization. Dry this crop at  $100^\circ$ – $110^\circ\text{C}$ . to constant weight. Cool in a desiccator and preserve in a tightly stoppered bottle. (The product has no water of crystallization and is not appreciably hygroscopic.) Prepare a solution containing 10 mg. of Pb per cc. in about 1% nitric acid, and from this solution make weaker dilutions as needed. Because lead tends to precipitate (probably as a silicate) from very dilute solutions,<sup>1</sup> the weaker dilutions should not be used over long periods.
- \***(43)** *Hydrochloric acid*.—(3+97).

#### PROCEDURE

*Preparation of Sample*.—Weigh ten apples (or pears, etc.) on a rough balance. Pull or cut out the stems at a point just below the skin and trim off the sepals (the dried-up residue of the blossom) with a sharp, narrow-bladed knife, so that the alkaline solvent has a clear unimpeded entrance into the calyx cup. Do not cut any more flesh than necessary. Allow the stems and sepals to fall into a large funnel, with a stem of sufficient size to prevent clogging, inserted into the neck of a 500 cc. volumetric flask. To 25 cc. of 30% NaOH in a 600 cc. beaker add 200 cc. of water and 25 cc. of 10% sodium oleate and heat to *gentle* boiling. Impale each fruit, in turn, upon a pointed glass rod, immerse it in the alkaline solution until the skin begins to check, and then remove to the funnel and rinse with a stream of hot  $\text{HNO}_3$  (1+49), being particular to flush out the stem and calyx ends thoroughly. When all the fruit has been thus treated, cool the alkaline solution somewhat and add it to the acid solution in the flask. Rinse beaker and funnel with water, cool, make to volume, and mix.

Into a 300 cc. Erlenmeyer flask place exactly 20 cc. of  $\text{HNO}_3$  (1+4). Mix the sample solution thoroughly, immediately withdraw 200 cc. in a pipet, and add it

<sup>1</sup> Bernhard, *Z. anal. Chem.* 67, 97 (1925).

to the acid in the Erlenmeyer while swirling vigorously. Filter on a rapid filter. (The filtrate must be clear. If the first portion is cloudy, return it to the filter until a clear filtrate is obtained.) Remove exactly 100 cc. to a 500 cc. tall-form beaker.

[The procedure outlined is unsatisfactory in the presence of manganese (fruit sprayed with manganese arsenate). Manganese hydroxides are precipitated by the alkali treatment; they occlude lead, and if in higher than divalent state may not be redissolved by the dilute acid used. The result is a large loss of lead in the filtration, which could be overcome by acidification with strong acid, and manganese in moderate amount would not interfere in the final color comparison. However, there are difficulties in handling the larger amount of electrolytes, occasioned by acidification with strong acid, because agglomeration of lead sulfide is more likely to occur. As the presence of manganese compounds may cause difficulties or uncertainties it is believed advisable to handle such samples by other methods. A method of testing for manganese in "strip" solutions is given later.]

*Determination.*—To the solution in the beaker add 3 or 4 glass beads and 10 cc. of bromine water and boil rapidly until the bromine is mostly expelled. Add 10 cc. more bromine water and again expel by boiling. When the color of the solution ceases to fade, cool to about 50°C., make alkaline with 2 cc. of 30% NaOH and add 1 cc. of 30% H<sub>2</sub>O<sub>2</sub>. Heat slowly to about 80°C. to promote oxidation. When foaming subsides, bring to boiling and evaporate rapidly to a volume of 15–20 cc. Cover the beaker with an inverted watch-glass (to wash down the sides with condensed steam), cool to about 50°C., and add 1 cc. of 30% H<sub>2</sub>O<sub>2</sub>. Again heat slowly over a small flame, allowing steam to escape by uncovering the lip of the beaker, until the major portion of the H<sub>2</sub>O<sub>2</sub> is decomposed. Complete the removal of the H<sub>2</sub>O<sub>2</sub> by boiling with 1 cc. of 30% urea for about 30 seconds. Remove the watch-glass and wash down the sides of the beaker with 5 cc. of HNO<sub>3</sub> (1+4). Boil for about 1 minute and add 2–3 drops of formic acid to destroy any remaining free bromine.

Cool, and transfer to a 125 cc. separatory funnel, limiting the volume to about 50 cc. Add 2 cc. of NH<sub>4</sub>CNS solution (35) and 20 cc. of amyl alcohol and shake vigorously; allow to stand until the alcohol layer is clear. (The aqueous layer is somewhat cloudy but should be colorless or nearly so. This extraction removes iron and in addition a small quantity of unoxidized coloring matter.) Draw off the aqueous layer slowly into a 100 cc. volumetric flask. Wash the alcohol once with 5 cc. of HNO<sub>3</sub>-NH<sub>4</sub>CNS solution (36), add the washings to the solution in the flask, dilute to volume, and mix. If the aqueous layer is distinctly colored after one amyl alcohol extraction, re-extract it as this solution must be perfectly clear and practically colorless. Draw it off into another separatory funnel, add 20 cc. of amyl alcohol, and shake. Wash both portions of alcohol with a single 5 cc. portion of the HNO<sub>3</sub>-NH<sub>4</sub>CNS solution (36).

To a 25 cc. aliquot in a 50 cc. Nessler tube (matched tubes are necessary), add 10 cc. of NH<sub>4</sub>OH-KCN-citrate solution (41) and 1 cc. of gum solution (38) and mix by inverting. (The cyanide forms a complex with copper which prevents precipitation of copper sulfide. The citrate will prevent precipitation of phosphates. The mixture should be perfectly clear.) Add 10 cc. of Na<sub>2</sub>S-gum solution (40), dilute to 50 cc., and mix gently by inverting and reversing three times. Compare the color developed to that developed by standard amounts of lead.

*Standards.*—If the colors developed are to be comparable, the same amount of electrolytes must be present in the standards as is present in the samples. The following quantities of reagents were calculated on the assumption that all reagents except rinse acid were carefully measured, and the rinse acid approximates 250 cc. Actually it may vary about 50 cc. to either side of 250 cc. without appreciably affecting the colors developed.



To 18.18 mg. of Pb (42) add 135 cc. of 30% NaOH, 372 cc. of HNO<sub>3</sub> (1+4), and 20 cc. of 30% urea. Cool, dilute to 1 liter, and mix.

Prepare a blank solution similarly, omitting lead.

Extract the iron from 50 cc. aliquots of the standard and blank as directed under "Determination" and dilute to 100 cc. volumes. These solutions will be known as the extracted standard and extracted blank, respectively.

The color of a sample that matches the color developed by a 25 cc. aliquot of the extracted standard indicates a lead content of 1 mg. in 100 cc. of the *original* sample solution.

To prepare other standards take smaller aliquots of the extracted standard solution and make up the deficiency (to 25 cc.) with the extracted blank solution.

Observe the colors by looking down the length of the tubes toward a white surface reflecting a north light, avoiding any shadows or unevenness of illumination, eye fatigue, etc. (Three compartment comparator boxes will be found convenient.) For rough preliminary comparisons the time elapsing between preparation of standard tubes and a sample tube may be as long as 30-45 minutes. However, the color does change with time because of agglomeration of the sulfide particles. For this reason, close readings can be made only if the standard tube is prepared at the same time as the sample tube.

If it is desired to use the sample solution for an arsenic determination by the Gutzeit method substitute HCl (3+97) for the HNO<sub>3</sub> (1+49) specified as a rinse, in this case using 30 cc. of HCl and 281 cc. of HNO<sub>3</sub> (1+4) instead of the 372 cc. of HNO<sub>3</sub> (1+4) specified in the standard and blank solutions. For the arsenic determination acidify 100 cc. of the sample solution with 10 cc. of strong HCl, filter, and use an aliquot of the filtrate in the Gutzeit generator. (The alkaline sample solution is always added to the acid with vigorous mixing, rather than the acid to the alkali, in order to avoid occlusion in the precipitated waxes. This removes oleic acid which would otherwise distinctly repress the evolution of arsine and cause low arsenic results.) Correct the Gutzeit standards for the reagents in the sample by adding to the standard generators the reagents occurring in the aliquot of the sample taken.

## DISCUSSION

The method requires from 2 to 3 hours for a single determination, but several samples may be carried along at the same time and the results obtained almost simultaneously in a somewhat longer period. The method has been applied to control work on an extended scale during the past season.

The accuracy of this method was checked by adding known quantities of lead (unknown to analyst, Vorhes) to the "strip" solutions of lead-free apples. The results obtained are given in Table 4.

TABLE 4.—*Recovery of lead from apple strip solutions*

ADDED grains/lb.	FOUND grains/lb.
0.008	0.010
0.023	0.024
0.017	0.017
0.028	0.030
0.012	0.012
0.016	0.015
0.015	0.015

Analysts interested in the colorimetric sulfide method as applied to apple "strip" solutions might find the photoelectric method of color comparison of Samuel and Shockey (p. 141) very useful.

#### V. ELECTROLYTIC METHOD (WICHMANN-CLIFFORD)

This method is based on electrolytic anodic deposition of lead as the peroxide from a dilute nitric acid solution, reaction of the peroxide with an acidified potassium iodide solution, and titration of the liberated iodine.  $\text{PbO}_2 + 4 \text{HI} = \text{I}_2 + \text{PbI}_2 + 2 \text{H}_2\text{O}$ .

Hillebrand and Lundell<sup>2</sup> state that the elements bismuth, antimony, tin, and manganese will separate on the anode as higher oxides and contaminate the lead peroxide deposit, and that halogens, arsenic, selenium, tellurium and phosphorus will prevent its deposition. Moderate quantities of the elements of the latter series expected in spray residues do not prevent complete deposition of lead by the method described. Bismuth, antimony, and tin are not found at present in commercial spray residues. Manganese is found, however, and must be removed before electrolysis.

Quantities of lead from 0.05 to 10 mg. or more may be very satisfactorily separated on the anode and titrated with 0.001 or 0.005 *N* thio-sulfate.

#### NEW REAGENTS

\*(44) *Potassium dichromate*.—C.P.

\*(45) *Sodium acetate solution*.—Saturated.

(46) *Potassium iodide solution*.—10% W/V. Dissolve 5 grams of the purest KI in CO<sub>2</sub>-free distilled water and dilute to 50 cc. Prepare as frequently as is necessary to prevent formation of sufficient free iodine to develop the starch-iodide color when mixed with acetic acid, sodium acetate, and starch solution as in preparation for titrating a blank.

(47) *Standard sodium thiosulfate solution*.—Prepare an approximately 0.005 *N* or 0.001 *N* solution by dilution of reagent (7) in the exact ratio of 1:20 or 1:100 with CO<sub>2</sub>-free distilled water. Standardize the dilute solution by running known quantities of pure lead (42) of the order 2–4 mg. or 0.2–0.5 mg., respectively. Prepare the dilute solutions at least semi-weekly. Since the 0.1 *N* solution is liable to change over long periods (particularly when freshly made), standardize at least once a month. As the dilutions are made in exact ratios, it is not necessary to standardize each time a dilution is made.

(48) *Potassium periodate*.—C.P. KIO<sub>4</sub>.

(49) *Phosphoric acid*.—Sirupy or 85%.

#### PROCEDURE

*Preparation of Sample (A—Solvent)*.—Proceed as directed in the colorimetric sulfide method (No. IV) to "... make to volume and mix."

Pipet exactly 25 cc. of strong, fresh HNO<sub>3</sub> into a 500 cc. Erlenmeyer flask. Mix the alkaline solution thoroughly, immediately withdraw 250 cc. by means of pipets,

<sup>1</sup> Jones, *Analyst*, 58, 11 (1933); Lucas and Grassner—*Emich Festschrift, Mikrochemie*, 197 (1930).

<sup>2</sup> *Applied Inorganic Analysis*, p. 182.

and add to the acid in the Erlenmeyer while swirling vigorously. Filter on a rapid filter. If the first portion is cloudy, return it to the filter until a clear filtrate is obtained.

Test for manganese as follows: To about 10 cc. of the filtrate in a small beaker add about 5 cc. of phosphoric acid (49) and about 0.2 gram of potassium periodate (48), and boil gently. Evaporate to a sirupy consistency, adding a little more periodate, if necessary, to decompose organic matter. Cool, and dilute with a few cc. of water. The pink color of permanganate ion appears if as little as 0.001 mg. of manganese is present.

If manganese is absent, neutralize 200 cc. of the filtrate in a 250 cc. beaker with strong ammonia; add 2 cc. of strong, fresh  $\text{HNO}_3$  and proceed as directed under "Electrolysis."

If manganese is present, eliminate it, because manganese dioxide deposits on the anode as does lead peroxide, reacts with KI, and gives a high figure for lead. Transfer 200 cc. of the filtrate to a 500 cc. short-stemmed separatory funnel and proceed as directed in Loughrey's method (No. III), beginning "Add 15 cc. 20% citric acid . . ." up to ". . . and evaporate to dryness," but omit the  $\text{KClO}_3$  and substitute a 250 cc. beaker for the 150 cc. beaker specified. (In the extraction with dithizone the small quantity of emulsion that usually forms at the junction of the two layers should be drawn with the last extraction into the smaller funnel where it will dissipate.)

To the dry residue in the beaker add 5 cc. of strong  $\text{HNO}_3$  and boil gently over a free flame while swirling. Fume for a few minutes in this manner, then add about 20 cc. of water, and boil vigorously, while swirling, for about 2 minutes, or until the solution is practically clear. (The rapid boiling removes most of the oxides of nitrogen formed in decomposing the organic lead compound.) Dilute to about 150 cc. (The partially decomposed dithizone changes color at approximate neutrality, yellow to orange.) Neutralize rapidly with strong ammonia from a buret, using this change of color as an indicator. (If desired a small piece of litmus paper may be used.) Add 2 cc. of strong, fresh  $\text{HNO}_3$  (water-white), dilute to about 200 cc., and electrolyze.

Always carry the lead determination through the dithizone extraction when a hydrochloric rinse and/or acidification is used in order to remove chlorides which interfere in the electrolysis, and wash the combined dithizone extract a second time with dilute ammonia to be sure that chlorides are removed.

The procedure described is subject to the limitations in efficiency of the solvent treatment mentioned in the colorimetric sulfide method.

**B—"Mush".**—Weigh 40–50 apples (or pears, etc.) on a rough balance. Peel the fruit, being careful to completely remove the stem and calyx ends. If a mechanical peeler is used, remove the stem and calyx ends before placing the fruit in position in order to avoid any danger of forcing spray residue from the end cavities into the flesh of the fruit. Weigh the peelings, including stem and calyx ends, and run them three times with thorough mixing through a food grinder that shears rather than presses, so that an homogeneous mush-like mass results without appreciable separation of liquid. Weigh 200 grams of the ground material into an 800 cc. beaker, dilute to about 300 cc., and add 40 cc. of strong  $\text{HNO}_3$ . Bring to a boil and stew slowly while stirring until initial foaming ceases and a comparatively smooth mixture results (about 10 minutes). Cool, transfer to a 500 cc. volumetric flask, make to volume and mix. (The volume occupied by the solid material of 200 grams of peelings so treated averages 15 cc.) Filter, remove a 250 cc. aliquot of the clear filtrate to a 500 cc. short-stemmed separatory funnel, and extract the lead with dithizone as directed under Method III, beginning "add 15 cc. of 20% citric acid. . . ."

This procedure quantitatively separates the lead from the fruit, and the use of a large sample reduces sampling error to a very low figure.

**C—Adaptation of the Wichmann-Murray and Loughrey Methods to Electrolytic Determination.**—Quantities of lead less than 1 mg. may be more accurately separated electrolytically than by a chromatating procedure because of the difficulty of handling small chromate precipitates. Furthermore, small quantities of iron, aluminum, phosphates and arsenates, such as would seriously interfere in obtaining a satisfactory chromate precipitate, do not interfere in this electrolytic determination. Bismuth, tin, antimony and manganese must be absent or removed before electrolysis. If wet-ashed solutions do not contain interfering metals or enough of the acid-forming, interfering elements to cause trouble, neutralize with ammonia, add 1% of nitric acid, and electrolyze direct, provided the lead sulfate is brought completely into solution. Dissolve the sulfides obtained in the Wichmann-Murray method with a few cc. of strong, hot  $\text{HNO}_3$  (instead of  $\text{HCl}$  (1+1) and  $\text{NaBrO}_3$ ), thoroughly rinse into a 250 cc. beaker with hot water, and boil the solution until colloidal sulfur is coagulated or oxidized. Neutralize the solution with strong ammonia, add 2 cc. of strong, fresh  $\text{HNO}_3$ , and bring the volume to about 200 cc. for electrolysis. Prepare the dry dithizone extract obtained in Loughrey's method for electrolysis as directed under "V, A-Solvent," beginning "To the dry residue. . ."

**Electrolytic Apparatus.**—Four dry cells connected in series constitute a convenient source of current. The meter should be substantial and accurate, but it need not be expensive; it can be conveniently mounted, along with a switch, fuse, rheostat, and a motor control resistance, on a transite panel. The current rheostat is a 60-ohm radio type. A small electric motor (1/20 h.p.) mounted on a ring stand clamp and equipped with a chuck and binding post is used to rotate the anode. A 110 volt universal type motor connected through a variable resistance of 25–500 ohm, 1/2 amp. capacity, has been found satisfactory. A motor of proper type for anode rotation may also be operated from a storage battery. The rate of rotation may vary from 400 to 800 r.p.m. The electrodes consist of: (A) a 45-mesh sand-blasted platinum gauze cylindrical anode 2"  $\times$  1/2" and 5" in overall length, the stem being of 14-gauge platinum wire, approximate weight 12 grams; (B) a cathode of 18-gauge platinum wire wound in spiral form and weighing 11–15 grams. An anode 1"  $\times$  5/16" and 5" overall length has been found very satisfactory for smaller quantities of lead.

The siphon is a glass tube bent to form an *N* shape with a hole in the lower bend. To start the siphon the finger is placed over this hole, and after the electrolyte has been sucked into the central portion, the finger is removed to allow the electrolyte to drain. A distilled water inlet fitted with a stopcock leads from a reservoir so as to play directly on the anode.

The insulated cathode support may be improvised by using a heavy glass rod mounted in a wooden base. On this is mounted, by means of an ordinary clamp, a brass rod fitted with a binding post at either end.

The set-up of the apparatus given in the sketch (Fig. 2) is merely suggestive. Arrangement of the units may be changed to suit the convenience of the analyst.

**Electrolysis.**—Immediately before electrolyzing bring the anode to red heat in the oxidizing flame of a Bunsen burner. (A somewhat variable blank is obtained, even when the purest reagents are used, if the anode is not heated just before the determination, due, possibly, to a film of oxygen adsorbed on the anode and activated during electrolysis. Heating reduces and renders constant this "oxygen" blank.)

In all methods of preparation for electrolysis the sample at this point is contained in a volume of about 200 cc. of approximately 1%  $\text{HNO}_3$  in a 250 cc. beaker.

Place the beaker in position in the apparatus, making sure that the electrodes are well covered with solution, and start the motor. Heat to  $60^{\circ}$ – $70^{\circ}\text{C}$ ., and add 0.2–0.3 gram of  $\text{K}_2\text{Cr}_2\text{O}_7$  to keep the solution in an oxidized state and to prevent the formation of nitrites. (Excess  $\text{K}_2\text{Cr}_2\text{O}_7$  should be present, particularly in the presence of organic matter. In this connection, it will be noted that fresh nitric acid has been specified in order to limit the amount of nitrites to a minimum.) Start the current and adjust it to 100–150 milliamperes and electrolyze with a moderately rapid rate of stirring at  $60^{\circ}$ – $70^{\circ}\text{C}$ . for 15 minutes. Then remove the flame, insert the siphon in the beaker, start the stream of distilled water playing directly on the revolving anode, and start the siphon to wash the acid from the beaker. Be careful to keep

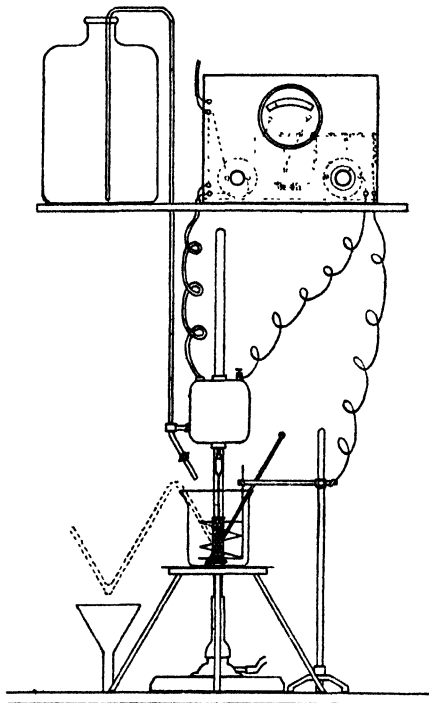


FIG. 2. ELECTROLYTIC APPARATUS

the level of the solutions above the deposit on the anode. (The acid is entirely removed when the current drops to zero. About 3 liters of distilled water will be required. If the quantity of distilled water is limited, the anode may be removed from the acid solution at the end of the electrolysis by carefully lifting motor and electrode, while rotating, through the stream of distilled water in such a manner that the electrolytic current is not broken, and the anode is progressively rinsed free from acid from the top downward. This operation requires less than 500 cc. of distilled water but it must be carefully carried out in order that none of the deposit is redissolved or the electrodes short-circuited.) Turn off the motor, electrolysis current, and rinse water, immediately remove the anode from the motor and rinse finally with distilled water. The conditions of electrolysis specified (low acidity, rotation of the anode, elevated temperature, and low current density)<sup>1</sup> are designed

<sup>1</sup> Jones, *Analyst*, 58, 11 (1933).

to counteract the interference of arsenic, phosphates, and chlorides, and to insure the complete deposition of small quantities of lead as  $PbO_2$ . The maximum allowable quantities of interferences are shown later in tables of results.

**Titration.**—During electrolysis, prepare in a lipped test tube or graduate  $5/8"$  in diameter and about 4" long the following mixture: 0.5 cc. of acetic acid, 1.5 cc. of saturated sodium acetate and 1 cc. of 10% KI diluted to a volume of 15 cc. Immerse the anode in this solution and mix by giving it a rotating motion. If the appearance of the deposit on the anode indicates a large quantity of lead (10–20 mg.) increase the quantity of sodium acetate and acetic acid. (No insoluble  $PbI_2$  should form and the deposit should dissolve completely and almost immediately.) Remove the anode to a similar tube or graduate containing 15 cc. of water. Transfer the iodide mixture to a 125 cc. Erlenmeyer flask, remove the anode from the second tube, rinse the first tube with its contents, and add to the solution in the Erlenmeyer. Repeat the rinsing. Titrate the liberated iodine immediately with 0.005 *N* thiosulfate solution from a buret with 0.05 cc., or smaller, divisions, using starch indicator. The end point is reached when the last faint starch-iodide color just disappears when the flask is held against a white background. Take care to avoid undertitrating, as this last faint shade is very easy to miss. (After a little practice the analyst can tell from the appearance of the electrode whether he will have a high or low titration.) If the quantity of lead is very low, add a few cc. of starch solution to the iodide solution immediately before immersing the anode in it, and reduce the amount of rinse water as low as is practicable. (Very dilute solutions of iodine react slowly with starch. When the quantity of lead is seen to be very small it is better to titrate directly into the stripping tube, using the electrode as a stirrer. This procedure is very useful with the smaller electrode and 0.001 *N* thiosulfate. About 5 cc. of stripping solution will cover the small electrode, and the total volume at the end of the titration should approximate 10 cc. The end point of the titration is seen by looking down the length of the tube against a white background. This makes a very delicate titration.)

Run all impurity blanks as well as "oxygen" blanks in the manner described and subtract from all determinations including standardizations.

**Calculation of Results.**—By standardizing the thiosulfate solution against pure lead, the factor is obtained directly in terms of mg. of Pb per cc. Use the following formulae for calculation of results:

#### Procedure A

$$\frac{(\text{Titer} - \text{blank}) \times \text{factor}}{\text{Wt. of sample (grams)}} \times 19.25 = \text{grains/lb.}$$

#### Procedure B

$$\frac{(\text{Titer} - \text{blank}) \times \text{factor} \times \text{wt. of peels (grams)}}{\text{Wt. of sample (grams)}} \times 0.0679 = \text{grains/lb.}$$

$$\text{Grains/lb.} \times 143 = \text{parts/million.}$$

## DISCUSSION

The "Mush" procedure has been described as applicable to fresh fruits that can be peeled, but no doubt this method of preliminary treatment could be adapted to many other products. Fischer has applied dithizone extraction to the separation of several metals from various biological ma-

terials. Emulsion formation may be the only drawback. If destruction of organic material<sup>1</sup> can be avoided, the time required for analysis can be materially shortened.

The factors that limit the electrolytic separation of  $\text{PbO}_2$  and the subsequent iodometric titration are the magnitude of the "oxygen" blank (proportional to the surface area of the electrode) and the delicacy of the iodometric titration. The character of the results that may be expected with the electrolytic method is illustrated in Tables 5, 6 and 7. In most instances, Tables 5 and 6, the analyst (Clifford) was unaware of the quantities of lead added.

TABLE 5.—*Recovery of lead by electrolytic method*

SAMPLE	LEAD ADDED mg.	ELECTROLYTIC METHOD USED	LEAD RECOVERED mg.
Lead solution—no interferences	0.036	A. Small electrode	0.037
	0.040	" "	0.040
	0.052	" "	0.052
	0.080	" "	0.080
	0.093	" "	0.095
	0.160	" "	0.156
	0.200	" "	0.197
	0.400	" "	0.395
	0.20	Large electrode	0.20
	0.50	" "	0.50
	0.70	" "	0.69
	1.03	" "	1.03
	1.95	" "	1.96
	3.59	" "	3.60
	4.75	" "	4.77
	7.83	" "	7.80
	10.03	" "	10.04
Strip solution from lead-free apples	1.32	" "	1.30
	2.00	" "	2.02
	3.02	" "	2.99
	3.19	" "	3.08
Ground peelings from lead-free apples	1.00	B. " "	1.00
	1.00	" "	1.01
	1.82	" "	1.80
	2.00	" "	1.96
	3.40	" "	3.29
	4.00	" "	4.02

The recoveries of lead in the presence of interfering substances by the electrolytic method are shown in Table 6.

The data given in Table 6 are useful to the analyst as they indicate the permissible limits of the interfering acid radicals during electrolysis.

TABLE 6.—*Recoveries of lead in presence of interferences*

CHARACTER AND AMOUNT OF INTERFERENCE mg.	ELECTRODE	LEAD ADDED mg.	LEAD RECOVERED mg.
2 P <sub>2</sub> O <sub>5</sub>	large	1.00	0.99
4 "	"	1.00	0.96
10 "	"	1.00	0.95
20 "	"	1.00	0.99
40 "	"	1.00	0.96
100 "	"	1.00	0.96
10 As <sub>2</sub> O <sub>3</sub>	"	1.00	0.98
10 "	"	10.00	9.80
10 NaCl	"	0.40	0.40
30 "	"	0.40	0.41
50 "	"	0.40	0.35
50 "	"	4.00	3.92
10 P <sub>2</sub> O <sub>5</sub>	small	0.05	0.049
30 "	"	0.05	0.049
50 "	"	0.05	0.037
1 As <sub>2</sub> O <sub>3</sub>	"	0.05	0.050
5 "	"	0.05	0.050
10 "	"	0.05	0.050
20 "	"	0.05	0.051
30 "	"	0.05	0.046
50 "	"	0.05	0.011
100 "	"	0.05	none
5 NaCl	"	0.05	0.052
10 "	"	0.05	trace
As <sub>2</sub> O <sub>3</sub> P <sub>2</sub> O <sub>5</sub> NaCl	large		
5 50 10	"	0.40	0.40
5 50 30	"	0.40	0.28
5 50 50	"	0.40	0.11
3.5 50 —	"	1.40	1.40
2.0 25 —	"	0.34	0.36
5.0 100 —	"	2.24	2.20

As thousands of analyses of lead were made last year in the field laboratories of the Food and Drug Administration, by other Federal and State agencies, and by the fruit growing industry itself on apples and pears by one or more of the preceding methods it seems sufficient merely to show a few of the first results obtained by Clifford and Vorhes on ground and mixed commercial apple peelings (Table 7).

TABLE 7

*Lead content of commercial apple peelings by different methods*

ELECTROLYTIC R grains/lb.	ASHING (II A), SULFIDING (II) ELEC- TROLYSIS OF NITRIC ACID SOLU- TIONS OF SULFIDES (V)
0.0730	
0.0725	0.0705
0.0695	
0.0164	
0.0174	0.0175



## VI. COLORIMETRIC DITHIZONE METHOD (VORHES-CLIFFORD)

This method is based on the pioneer work of Emil<sup>1</sup> and Hellmut Fischer<sup>2</sup> with diphenylthiocarbazon. It was originally devised for rapid approximate determinations on fresh apples and pears, and especially to avoid some of the interferences that were troublesome in previous methods. As written it should be very satisfactory for routine work, and with certain refinements it can be made very exact even for exceedingly minute quantities of lead.

The solvent method of spray-residue removal is utilized. Limitations of this method are discussed under the colorimetric sulfide method (No. IV). The method should give results accurate to 0.001 grain/lb. within the range of 0–0.025 grain/lb. In speed and simplicity it surpasses the other methods presented, and it is subject to none of the common interferences known to affect them.

When a chloroform or carbon tetrachloride solution of diphenylthiocarbazon (dithizone) is shaken with progressively larger amounts of lead in ammoniacal cyanide solution, its normal green color changes, through a series of blues, purples, and crimsons, to a cherry red. This gradual change in color is caused by the formation of a red, chloroform-soluble organic lead compound. The combination in varying proportions, depending on the relative amounts of lead present, of this red color with the blue-green of the excess dithizone produces the intermediate colors.

## NEW REAGENTS

\*(50) *Ammonia-potassium cyanide-citric acid solution*.—Dissolve 10 grams of KCN and 10 grams of citric acid in 500 cc. of strong ammonia and dilute to 1 liter. Preserve the solution in a dispensing apparatus that will minimize loss of  $\text{NH}_3$  by volatilization.

\*(51) *Dithizone solution*.—Dissolve 50 mg. of purified dithizone in 1 liter of chloroform and "standardize" by dilution as directed under "Standards." Preserve in a dispensing apparatus that will prevent evaporation.

*Preparation of Sample*.—With a 1400 gram sample, proceed as directed in the "Colorimetric Sulfide Method" (No. IV), to "—make to volume and mix."

In a 300 cc. Erlenmeyer flask place exactly 10 cc. of strong nitric or hydrochloric acid. Mix the sample solution thoroughly, immediately withdraw 100 cc. in a pipet, and add to the acid in the Erlenmeyer flask, while swirling vigorously. Filter on a rapid filter. If the first portion of the filtrate is cloudy, return it to the filter until a clear filtrate is obtained.

*Determination*.—Remove 20 cc. portions of the filtrate to each of three Nessler tubes (sets of at least 12 tubes matched for uniformity of color and diameter are necessary). First add 10 cc. of the ammonia reagent (50) to each tube; then to one tube add 20 cc. of the "standardized dithizone" solution (see "Standards") and to the others, 20 cc. of chloroform. Shake the tubes vigorously and allow the layers to separate. With a tube of clear chloroform backing the sample tube containing the dithizone, and one sample tube containing chloroform backing each of two standard

<sup>1</sup> *Ann.*, 190, 67 (1878); 212, 316 (1882).

<sup>2</sup> *Z. angew. Chem.*, 42, 1025 (1929); 46, 442 (1933); *Wiss. Veröff. d. Siemens Konzern*, 12, 44 (1933); *C.A.*, 27, 3418 (1933).

tubes, compare the color in the lower layer of the sample with that of the standards, looking through the tubes at right angles to their lengths toward a strong diffused light. (A comparator box, similar to the boxes used in colorimetric pH measurements but of larger size, will be found convenient.) A slight turbidity is produced in the sample tube (when working with apple strip solutions), which somewhat changes the color observed. To correct for this effect, introduce the same turbidity in the field of view of the standard tubes by backing them with sample tubes made up exactly as is the sample, except that chloroform is substituted for the dithizone solution.

*Standards.*—Introduce into each of two 1-liter volumetric flasks 47.5 cc. of 30% NaOH and the quantity and kind of acid indicated in the table below, according to the rinse and acidification to be used on samples:

RINSE	SAMPLE	ACIDIFICATION	STRONG HNO <sub>3</sub> cc.	STANDARD	STRONG HCl cc.
HNO <sub>3</sub> (1+49)		HNO <sub>3</sub>	100		
HCl (3+97)		HNO <sub>3</sub>	91		13.6
HNO <sub>3</sub> (1+49)		HCl	9		91.0
HCl (3+97)		HCl			104.6

To one of the flasks add 9.82 mg. of Pb in the form of standard lead nitrate (42). Mark this flask "standard" and the other "blank." Dilute both solutions to volume at room temperature and mix. (These two solutions contain the reagents in the proportion in which they occur in an acidified and filtered sample solution. The standard is equivalent in lead content to an acidified solution from a sample of 1400 grams carrying a lead load (removable by the solvents used) of 0.027 grain/lb. By a combination of the two solutions in suitable proportions the equivalent of any lead load from 0 to 0.027 grain/lb. may be obtained.

The standard tubes may be made up in intervals corresponding to 0.003 grain/lb. and then interpolation of the sample to 0.001 grain/lb. is conveniently made. The following table gives the quantities of "standard" and "blank" used in the Nessler tubes for each interval. They are conveniently measured into the tubes by means of burets.

GRAIN./LB.	STANDARD cc.	BLANK cc.
0.000	0.0	20.0
0.003	2.2	17.8
0.006	4.5	15.5
0.009	6.7	13.3
0.012	8.9	11.1
0.015	11.1	8.9
0.018	13.3	6.7
0.021	15.5	4.5
0.024	17.8	2.2
0.027	20.0	0.0

Standardize the dithizone as follows: Prepare standard 0.024 and 0.027 tubes and add 10 cc. of the ammonia reagent (50) to each. Then, from a buret, add to each tube in equal increments of 1 cc. or less, the dithizone solution (51), shaking vigorously between additions. Continue until the 0.027 tube is colored a cherry red, but the 0.024 tube shows the first hint of purple, noting carefully the volume of dithizone used when this end point is reached. Dilute each tube with sufficient chloroform to make a total of 20 cc. in the chloroform layer, shake, and observe the colors again to be sure that the 0.027 tube remains a cherry red and the 0.024 tube has a slight

purple or bluish tint, which will indicate that insufficient dithizone has been added to the 0.027 tube to react with all the lead, but that a slight excess is present in the 0.024 tube. Dilute the dithizone solution in such proportion that 20 cc. will contain the required quantity of dithizone to give a slight excess in the 0.024 tube and a deficiency in the 0.027 tube.

To each standard tube add, in the following order, 10 cc. of the ammonia reagent (50) and then 20 cc. of the standardized dithizone. Shake vigorously and allow the layers to separate. Stopper each standard tube securely with a new cork stopper. To avoid any slight error in dilution of the dithizone solution, do not use the tubes in which the dithizone was standardized.

### DISCUSSION

Many metals combine with dithizone under certain conditions, but the ammoniacal cyanide solution will prevent interference from all metals that are liable to be encountered in spray residues. The known interfering elements according to H. Fischer<sup>1</sup> are bismuth, stannous tin, and thallium.

The colors obtained with this method differ from those generally obtained in colorimetric work, in that their principal variations are in terms of color tint rather than of color intensity. Actually the amounts of the two colors in the mixture vary in inverse proportion, the blue decreasing and the red increasing with increasing quantities of lead. With the usual colorimetric methods the greatest sensitivity is obtained when the amount of color change corresponding to one unit change of the standard is a large percentage of the total color present. Similarly, in Method VI, when the quantity of lead is small, the difference of color between steps is most noticeable because, although the predominant color is blue, the amount of red corresponding to each step is a large proportion of the total red present. However, the differences in color are again quite noticeable in that range in which the dithizone is almost saturated with lead because, although the predominant color is red, the proportional variation of blue for each step is great. Thus, instead of sensitivity decreasing as color increases, as ordinarily expected, the sensitivity of this method first decreases and then increases with increasing quantities of lead. Therefore, the analyst engaged in spray residue control work will find it highly desirable to so place this second range of high sensitivity that it will cover the point in which he is most interested, namely, the "tolerance." This may be done by "standardizing" the dithizone solution, that is, adjusting its strength, so that the quantity used becomes saturated with lead at a point just above the tolerance figure.

If tightly stoppered, the standard tubes should not change color appreciably for two days, but they should be checked daily. It is obvious, however, that any considerable evaporation from the dithizone solution will change its strength and make impossible comparison of a sample pre-

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<sup>1</sup> *Loc. cit.*

pared some time later than the standards. Furthermore, the alkalinity of the aqueous layer, that is the  $pH$  of sample and standards, must be practically the same. The optimum  $pH$  under varying conditions has not yet been determined, but it is believed to be secondary to the equality factor of the  $pH$ . The ammonium compound of dithizone is colored an orange red and is soluble in water. Chloroform also has a great affinity for dithizone. Therefore, there is a partition of uncombined dithizone between the aqueous and chloroform layers, with the balance in favor of the chloroform if the excess quantity of ammonia is kept small. This partition necessarily exerts an influence on the final color of the chloroform layer, but as long as it is the same in standard and sample, accurate color comparisons can be made. The proportions of reagents given are empirical, but they have been found experimentally satisfactory for the quantities of lead usually found in spray residues. Because the  $pH$  of the aqueous layer is affected by all reagents used except the dithizone, they must be carefully measured and their concentration protected from changes due to evaporation. Slight variations in the volume of rinse acid used have not been found to affect the colors appreciably, but it is well to approximate 250 cc. as closely as is practicable.

For other than spray residue work, the analyst may find it advisable to readjust the concentrations of ammonia and buffer solutions to the amount of lead expected, which factor also governs the strength of dithizone. For example, if the lead is 0.01 mg. or less, the ammonia and dithizone concentrations must be restricted below those given above, while with 0.2 mg. both can be increased. The analyst should use his judgment.

An arsenic determination by the Gutzeit method or a check lead determination by the electrolytic method may be made on the sample solution used for this determination. It must be remembered, however, that nitric acid must be excluded from the Gutzeit determination and hydrochloric acid from the electrolytic. Therefore if the arsenic determination is desired a hydrochloric acid rinse is used, but if the electrolytic check is to be made, it is necessary to use the nitric acid rinse or the dithizone extraction procedure.

## RESULTS

The character of the results that may be obtained on fruits by Method VI in a period of approximately 30 minutes is indicated in Table 8. The quantity of lead added to "strip" solutions of lead-free apples was not known to the analysts, one of whom was trying the method for the first time.

## PERMUTATIONS AND POSSIBILITIES

Sources of lead other than spray residue have been given only passing attention, because the spray residue problem was so pressing. The diagram presents some of the permutations investigated but it does not indi-

TABLE 8

*Recovery of lead from lead-free "strip" solutions by dithizone method*

ANALYST	LEAD ADDED grains/lb.	LEAD FOUND grains/lb.
J. B. Wilson <sup>1</sup>	0.005	0.004
	0.010	0.010
	0.017	0.018
	0.021	0.021
P. A. Clifford	0.0085	0.008
	0.013	0.014
	0.020	0.020
F. A. Vorhes	0.0137	0.014
	0.0075	0.0075
	0.0225	0.024

cate further possibilities in preparation of samples, isolation or determination of lead, or substances not investigated by the writers. If destruction of organic matter can be avoided, for example, by the "mush" method, the time required for analysis will be materially shortened. After mashing, instead of using an electrolytic determination after separation with dithizone, the analyst could, no doubt, determine the lead directly by the colorimetric dithizone method. This method can be made extremely delicate by limiting both the volume and concentration of the reagent to increase the sensitivity at the expense of range. For example, 0.001 mg. of lead has been detected and determined quantitatively with 5 cc. of a chloroform dithizone solution containing 12.5 mg. per liter. The upper limit of the standard in this case was 0.02 mg., with 10 decided steps in the range. There is no reason to believe that 0.001 mg. is the lower limit, provided lead-free chemicals and chemical ware can be obtained or prepared and the color is viewed through a column the depth of which is greater than the diameter of a Nessler tube. It is believed that "two-color" colorimetry has advantages over other colorimetric methods. Volumetric methods for the determination of lead<sup>2</sup> and also of copper and mercury involving titration with dilute dithizone also appear available in the near future. The green color of dilute dithizone solution is so intense that the smallest excess in a small volume of chloroform or carbon tetrachloride is readily detected as an end point.

The only serious common interferences of the dithizone method are those of tin and bismuth. The latter is probably of most interest to biochemists, toxicologists, and the medical profession. Work designed to remove tin, antimony and bismuth interferences prior to the electrolytic and dithizone determinations is under way. If successful, it should enable the analyst to determine quite rapidly the lead in urine, feces, and biological materials in general. The limiting factors of the electrolytic sepa-

<sup>1</sup> Food and Drug Administration, Washington, D. C.<sup>2</sup> Bohnenkamp and Linnenweh, *Deut. Arch. Klin. Med.*, 175, 157 (1933).

ration and iodometric determination of lead are the magnitude of the anode or "oxygen" blanks and the accuracy of iodometric titrations. The oxygen blank appears to be proportional to the surface area of the anode. Reduction of the size of the electrode and proportionate reduction of the volume of the solution and of the current will determine smaller quantities of lead. The smallest quantity of lead so far determined (with the surprisingly small error of only  $\pm 2$  per cent) is 0.05 mg. No doubt the minimum determinable quantity of lead could be materially lessened if the size of the anode were reduced to that of a rotating sand-blasted stout platinum wire. The iodometric titration could also be improved if the volume to be titrated were kept at a minimum, and more dilute thiosulfate solutions and microburets used. It is not expected that the electrolytic method will determine lead in as minute quantities as does the colorimetric dithizone method, but the personal equation will not be so prominent. The latter method has been successfully used by the writers to determine quantities of lead (first separated by the electrolytic method) that could not be seen on a  $1" \times 5/16"$  electrode. The permutations between the electrolytic and dithizone methods of separation and determination appear to be numerous. The path to practical, rapid and accurate methods for the determination of small quantities of lead in foods, toxicological or biological products, seems to follow the routes described in this paper and particularly those involving electrolytic or dithizone estimations.

### SUMMARY

Six methods for the determination of small quantities of lead, particularly in spray residues, are described. They are presented in the order in which they were developed, and their practicability increases in about the same order.

## TURBIDITY AND COLOR MEASUREMENTS<sup>1</sup>

### I. A PHOTOELECTRIC CELL ARRANGEMENT FOR MEASURING SMALL QUANTITIES OF CERTAIN IMPURITIES IN REAGENT CHEMICALS

By R. A. OSBORN (Food Research Division,<sup>2</sup> Bureau of Chemistry and Soils, U. S. Department of Agriculture, Washington, D. C.)

It is the purpose of this paper to describe a relatively simple and inexpensive photoelectric cell set-up for the determination of such small quantities of impurities as may be found in reagent quality chemicals.

<sup>1</sup> Presented at the Annual Meeting of the Association of Official Agricultural Chemists, November, 1932.

<sup>2</sup> Food Research Division Contribution No. 208.

The principles of the "Speerschicht" or boundary type of photoelectric cell and its applications have been fully discussed.<sup>1</sup> No attempt will be made to cover the bibliography of this subject. It is believed that some of the features in the design and arrangement of the apparatus described here are original.<sup>2</sup> The data obtained by the use of this instrument illustrate its applicability, but they also indicate the difficulties of developing a reproducible technic for the measurement of small quantities of certain turbidities.

#### DESCRIPTION OF APPARATUS

The apparatus consists of a photoelectric cell (Weston Model No. 594) connected only to a 0-50 microammeter graduated in 50 divisions, with resistance of 103 ohms. The cell is mounted in a light-proof compartment with sliding double chamber for holding the tubes. The chamber slides horizontally and is provided with the necessary stops to permit ready centering of either tube between lamp and cell. The light source is a 32-candle-power automobile lamp, which is shielded and so mounted that it can be brought to a fixed position directly over the measuring tubes. Current is obtained from a heavy duty, lead storage battery, which is "floated" on the line with a double throw switch, to permit charging the battery at a rate slightly less than the discharge rate required during use, and also at a very low rate, which is just sufficient to prevent the battery from sulfating during periods when not in use. The voltage of the battery, which is readily observed by means of a voltmeter (0-8 volts), is maintained at approximately 5.8 during use. A variable rheostat of 0 to 0.75 ohm capacity is placed in series with the lamp circuit in order to increase or decrease the intensity of the light from the lamp as desired.

The reference tube and measuring tube are of the same size (2 cm. outside diameter and 25.4 cm. length) with optical glass disks sealed on the bases of both and on the top of the reference tube, which has a side arm to permit filling with distilled water. It was found desirable to grind that portion of the disks with which contact was made before sealing. While de Khotinsky cement made a satisfactory seal, a glycerol-phthalic anhydride resin recommended by Sager and Kennedy<sup>3</sup> was thought to be better. The volume of the measuring tube when filled, covered with the optical glass and ready for measurement, is a few drops less than 50 ml.

#### MEASUREMENT OF TURBIDITIES

The specifications by the Committee on Analytical Reagents of the American Chemical Society<sup>4</sup> in general provide for a visual comparison

<sup>1</sup> Circ. C-2-25 M., July, 1933, Weston Elec. Instrument Corp., Newark, N. J.; Muller, *Mikrochem.*, 11, 353 (1932).

<sup>2</sup> The writer takes this opportunity to thank John Hoffman, machinist, for offering many useful ideas in the design and construction of this apparatus and also B. A. Brice, Associate Physicist, for helpful suggestions.

<sup>3</sup> *Physics*, 1, 352 (1931).

<sup>4</sup> W. D. Collins, et al, *Ind. Eng. Chem. Anal. Ed.*, 5, 289 (1933). Ten additional references given.

of the turbidity, color, etc. produced by a definite amount of a standard solution of the impurity to be determined with that produced by a given weight of the reagent in question when the standard and the reagent are subjected to a nearly identical procedure. It is recognized that there may be present in the chemical being examined other substances that will react with the reagent for developing the precipitate or color and that other effects may influence the nature and amount of color or turbidity produced. Consideration was given to these factors when the limits for the amounts of the several impurities permissible in reagent chemicals were established. The specifications merely provide limits for the substances being examined, the total turbidity being credited to iron, lead, chloride, etc. This precedent is followed here.

Turbidities have been developed by following a definite procedure and using a series of aliquots of a standard solution. Data obtained permit construction of a curve representing the transmittance (or percentage of light which is not obscured in the measuring tube) of each aliquot. Reagents being tested for these impurities are subjected as nearly as possible to the same procedure. As blank determinations vary from week to week or month to month and indicate that the distilled water and possibly the reagents involved in the determinations are not strictly constant, it is considered advisable to regard the curves only as useful as approximations of the amounts of impurity. When greater accuracy is desired, standards should be prepared to contain amounts of the constituent suggested by first obtaining the transmittance of the sample being tested and consulting the previously established curve.

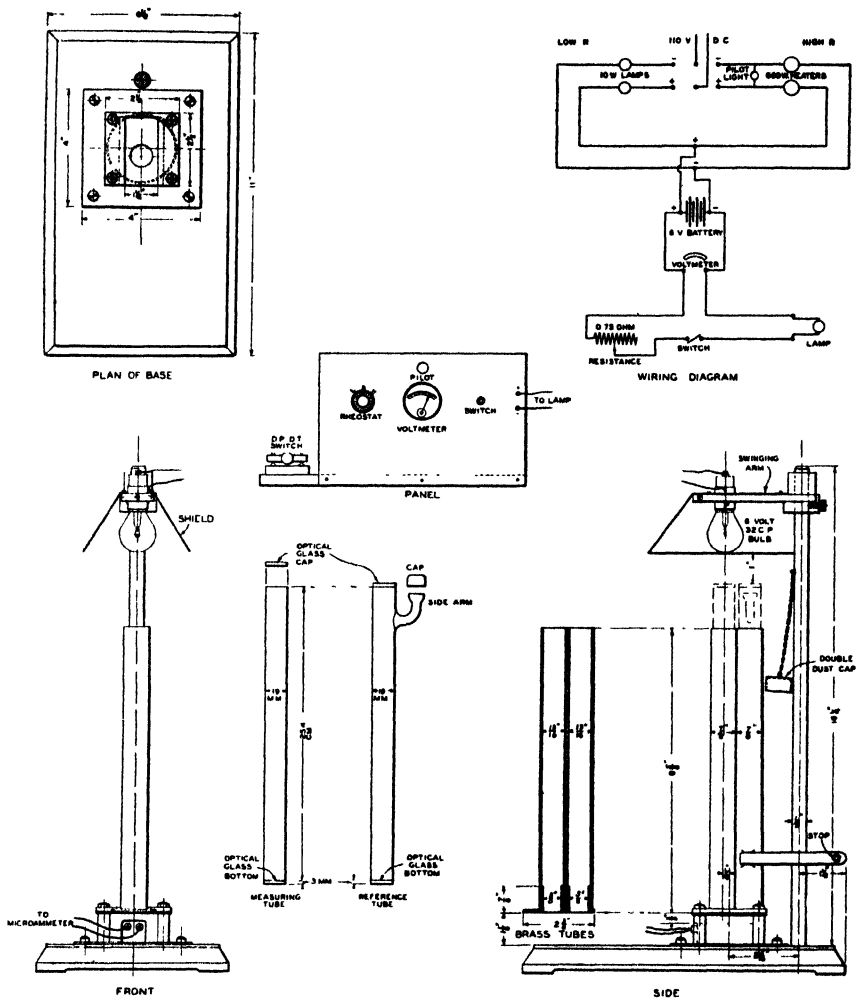
#### DETERMINATION OF THE "CONSTANT" FOR THE MEASURING TUBE

Fill the reference tube with distilled water, place in the rear chamber, and leave it there during all measurements. Fill the measuring tube with distilled water, cover, and insert in the front chamber. Pass the light through the reference tube to the cell for several minutes to obtain cell equilibrium. Record rapid alternate micro-ampere readings when the tubes are brought between the lamp and cell, and determine the constant of the measuring tube by simply dividing the reference tube reading by the measuring tube reading. It is necessary to redetermine the constant for the measuring tube before a new turbidity measurement can be made.

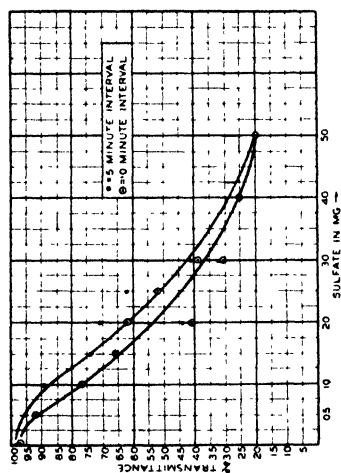
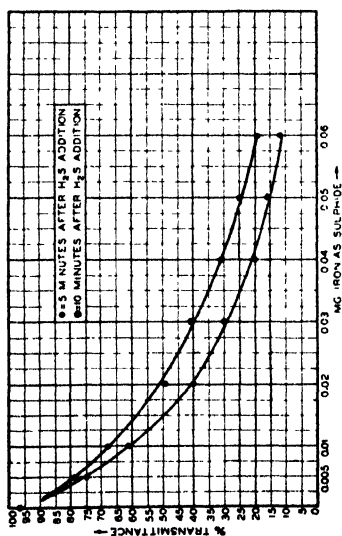
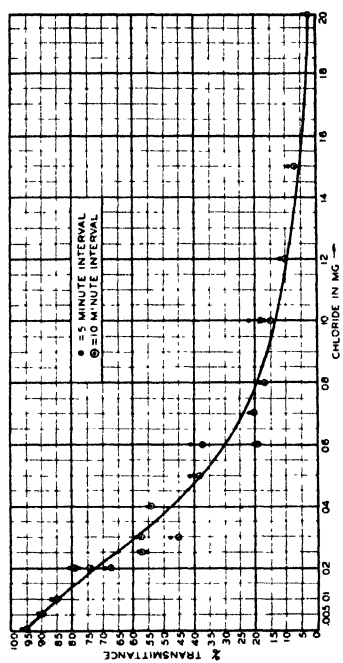
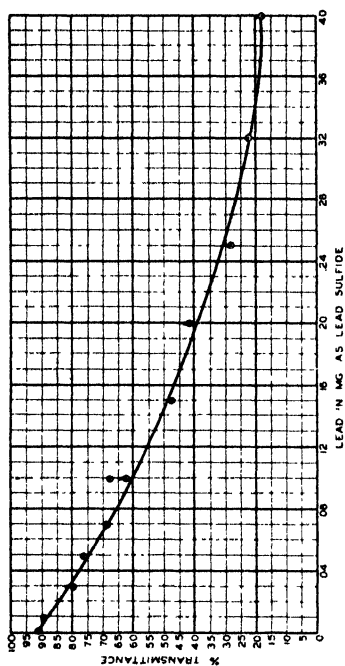
#### PROCEDURE FOR IRON AS SULFIDE

Place aliquots of a standard iron solution representing 0.005, 0.01, 0.02, 0.03, 0.04, 0.05 and 0.06 mg. of iron into clean, 250 ml. Pyrex beakers, and add distilled water to make the total volume in each beaker approximately 39 ml. Include a blank of distilled water. Add one ml. of ammonium hydroxide to each and mix by rotation. Determine the constant for the measuring tube as described previously. Rotate the contents of one of the beakers while adding to it 5 m. of freshly prepared saturated hydrogen sulfide water and mix for 15 to 30 seconds, using an interval time clock. Pour into the empty measuring tube, add distilled water until the tube is rounding full, empty the contents of the tube into the original container, and mix by rotation. Finally return to the measuring tube, cover, wipe dry, and insert in





INSTRUMENT TO MEASURE VARIATIONS IN COLOR AND TURBIDITY



the chamber of the instrument. Make readings similar to those taken during the determination of the measuring tube constant at 5 and 10 minute intervals. Calculate transmittance for each interval by multiplying the measuring tube readings by the constant and dividing by the reference tube readings. Then empty the measuring tube, rinse thoroughly, fill with distilled water, and determine its constant before proceeding to the measurement of the transmittances of the other standards.

The accompanying curves are typical of the behavior of several substances. The data were obtained by following a technic similar to that described for iron, differing only in the reagents employed and in the amounts of the standards taken as aliquots for measurements.

TABLE 1  
*Per cent transmittance of iron and lead as sulfide*

AMOUNT	IRON		AMOUNT	LEAD	
	5 min.	10 min.		5 min.	10 min.
Blank	97.0	97.0	Blank	90.6	89.8
<i>mg. Fe</i>			<i>mg. Pb</i>		
0.005	78.5	75.4	0.01	89.4	88.9
0.01	67.8	61.4	0.03	81.7	78.8
0.02	49.2	40.0	0.05	76.3	76.0
0.03	40.7	30.1	0.10	67.5	67.5
0.04	31.0	19.8	0.10	64.1	62.4
0.05	25.2	16.1	0.15	47.5	47.4
0.06	18.8	11.9	0.20	41.8	41.2
			0.25	27.7	27.5
			0.32	21.9	22.0
			0.40	18.2	17.8

TABLE 2  
*Per cent transmittance of sulfate as barium sulfate*

AMOUNT	TIME		TIME	TIME
	5 min.	10 min.	15 min.	20 min.
Blank	97.5	96.7		
<i>mg. SO<sup>4</sup></i>				
0.05	95.0	91.6	84.3	79.5
0.10	89.1	77.2	73.5	68.6
0.15	74.0	65.8	62.3	60.0
0.20	70.7	61.6		
0.20	44.1	41.3	40.7	40.3
0.25	61.8	51.7	48.9	48.4
0.30	32.4	30.7		
0.30	40.8	38.5	38.4	37.3
0.40	25.9	25.8	25.7	25.7
0.50	19.7	19.6		

TABLE 3

*Per cent transmittance of chloride as silver chloride*

AMOUNT	TIME	
	5 min.	10 min.
Blank	95.5	95.7
<i>mg. Cl</i>		
0.0025	90.8	90.7
0.0025	92.3	92.0
0.005	90.5	90.1
0.01	87.4	85.0
0.02	81.4	78.5
0.02	77.7	74.4
0.02	68.8	67.4
0.025	57.8	57.2
0.025	57.3	56.1
0.03	58.5	56.7
0.03	45.7	45.0
0.04	55.0	54.2
0.05	40.2	37.8
0.06	19.9	18.9
0.06	41.2	36.8
0.07	21.5	20.7
0.08	18.2	16.7
0.10	16.8	14.6
0.10	22.3	18.2
0.12	11.7	10.3
0.15	8.8	6.9
0.20	5.7	4.3

## SUMMARY

A photoelectric cell arrangement for measuring small quantities of certain impurities in reagent chemicals is described. Measurements for iron, lead, chloride, and sulfate are presented. Satisfactory measurements were obtained for iron and lead as sulfides, but difficulties were encountered in the measurement of sulfate and chloride.

# A RAPID AND ACCURATE PHOTOMETRIC METHOD FOR DETERMINATION OF LEAD IN SMALL QUANTITIES<sup>1</sup>

(Especially applicable to determinations of lead in spray residues and in food products.)

By BOYD L. SAMUEL and HOWARD H. SHOCKEY<sup>2</sup> (Division of Chemistry, Department of Agriculture, Richmond, Va.)

The method described makes use of the precipitation of lead as the sulfide and the determination photometrically by means of a photo-electric

<sup>1</sup> Presented at the Annual Meeting of the Association of Official Agricultural Chemists, held at Washington, D. C., November, 1933.

<sup>2</sup> Formerly with the Virginia Division of Chemistry, but now with the National Fruit Products Company, Winchester, Va.

cell. It should fill the need for a rapid and accurate method for determining small quantities of lead in food products. Bismuth and mercury are the only common metals that interfere. The method was worked out primarily to determine lead in spray residues on apples. It also proved to be quite satisfactory on apple pomace, jelly, vinegar, etc., and it should be easily adaptable to a wide range of materials that can be wet-digested when lead is present in small quantities.

#### PRINCIPLES OF METHOD

The apple peelings are wet-ashed with nitric and sulfuric acids, and most of the nitric acid is driven off by evaporation with water.<sup>1</sup>

The arsenic is distilled<sup>2</sup> as arsenic trichloride and then determined by either the bromate<sup>3</sup> or Gutzeit method.

Ferric iron, the most serious interfering element, is extracted from an aliquot of the residue from the arsenic distillation with ammonium thiocyanate and ether.<sup>4</sup>

The extracted aliquot is made alkaline with ammonium hydroxide; potassium cyanide is added to form colorless compounds with ferrous iron, copper, nickel, and cobalt; and ammonium citrate is added to prevent the precipitation of phosphates and calcium.<sup>5</sup>

The sample is transferred to the Nessler tube of the photo-electric colorimeter, and the apparatus is adjusted to take care of any turbidity in the solution. The lead is precipitated with sodium sulfide solution, and the quantity is determined from the meter reading by reference to a previously prepared graph of standards.

#### REAGENTS

- (a) *Ammonium thiocyanate solution*.—C. P. Saturated.
- (b) *Ethyl ether*.
- (c) *Nitric acid*.—C.P. Concentrated.
- (d) *Ammonium acetate*.—20 grams in 100 cc. of water.
- (e) *Ammonium hydroxide*.—C.P. Concentrated.
- (f) *Ammonium citrate solution*.—Dissolve 25 grams of C.P. citric acid in 50 cc. of water, make alkaline with ammonium hydroxide, and make to 100 cc.
- (g) *Potassium cyanide solution*.—C.P.—10%, alkaline with ammonium hydroxide.
- (h) *Sodium sulfide solution*.—C.P. 10% in water.
- (i) *Ammonium hydroxide-Potassium cyanide-Citrate solution*.—To 1 liter of C.P. ammonium hydroxide add 125 cc. of reagent (f) and 50 cc. of reagent (g).
- (j) *Standard lead solution*.—0.2374 gram of lead acetate,  $\text{Pb}(\text{C}_2\text{H}_3\text{O}_2)_2 \cdot 3 \text{H}_2\text{O}$ , per liter. 1 cc.  $\approx$  0.002 grains of Pb.
- (k) *Hydrazine sulfate solution*.—20 grams of  $\text{N}_2\text{H}_4 \cdot \text{H}_2\text{SO}_4$  and 20 grams of NaBr per liter of HCl (1+4).
- (l) *Sodium chloride*.—Commercial grade free from iodide is satisfactory.

<sup>1</sup> *Methods of Analysis*, A.O.A.C., 1930, 307.

<sup>2</sup> *Ibid.*, 37.

<sup>3</sup> *This Journal*, 16, 76 (1933). See also report of Associate Referee for 1933.

<sup>4</sup> *Hammett, Analyst*, 57, 822 (1932).

<sup>5</sup> Yoe, *Photometric Chemical Analysis*, 253; Scott, *Standard Methods of Chemical Analysis*, 4th Ed., 282.

## APPARATUS

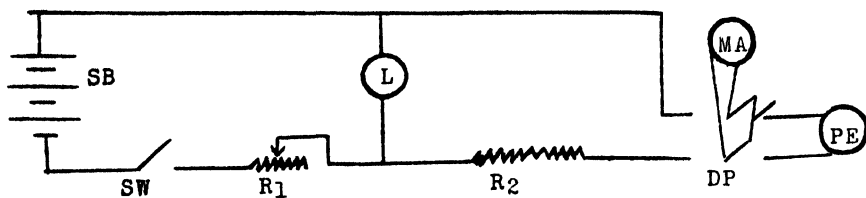


FIG 1.—SCHEMATIC DIAGRAM

SB 6-volt storage battery.

SW On-off toggle switch.

R<sub>1</sub> 1-ohm variable resistor capable of carrying 5 amperes of current.

R<sub>2</sub> 100,000-ohm resistor.

L 6 volt, 32-candle power automobile bulb.

DP Double pole-double throw toggle switch.

MA 0-100 micro-ammeter.

PE Weston Photronic cell, Model 594, without a center "dead" spot.

The colorimeter was built in the laboratory at a very small cost.<sup>1</sup> The instrument consists of a wooden box with the parts mounted as shown. The front opens on hinges to give access to the Nessler tube (N), which fits into a hole with a flange

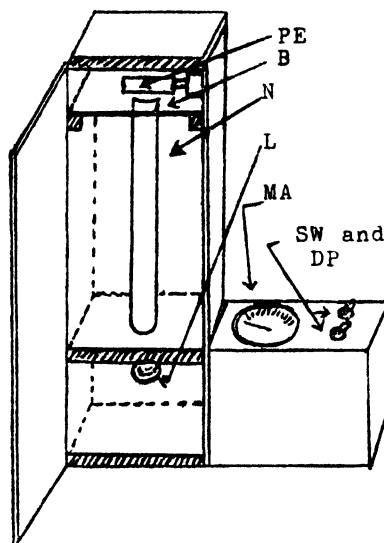


FIG. 2.—FRONT VIEW OF INSTRUMENT

<sup>1</sup> This colorimeter is a modification of one described by John H. Yoe and Robert H. Kean at the Virginia Academy of Science meeting, May 5, 1933. Further modification of Dr. Yoe's photoelectric colorimeter is now being made at the University of Virginia and will be described by him in a subsequent paper.

at the bottom just large enough to support it; it also fits snugly at the top in a bakelite strip (B), which slides in or out to allow removal. When the door is closed the bakelite strip is pushed all the way in, and the Nessler tube is held in the same position always. A scratch on the Nessler tube and on the bakelite strip provides for setting the tube in the same position each time. The bulb (L) is mounted at the back about  $\frac{1}{2}$  inch directly under the Nessler tube. The meter and switches are mounted in a compartment on the right. The 1-ohm rheostat is mounted on the back of the meter compartment. The switch SW (Fig. 1) turns the instrument on or off. The switch DP, when switched to the photo-cell, reads the micro-amps generated by the cell. When it is switched the other way it reads the voltage on the bulb (L). With the resistance employed ( $R_x$ ) 10 volts gives full scale deflection; the voltage reading then is one-tenth the meter calibration.

#### PROCEDURE

Wet-ash the peel from one pound of fruit (or convenient sized sample when other material is used) with nitric and sulfuric acids, and expel most of the nitric acid by evaporation with 50 cc. of water. After evaporation to white fumes allow the sample to cool and add 25 cc of distilled water. Now add 25 cc. of the hydrazine sulfate (k) and 20 grams of sodium chloride to the sample and distil<sup>1</sup> off the arsenic chloride. Titrate the arsenic in the distillate with standard potassium bromate solution or run by the Gutzeit method.

Wash the residue in the Kjeldahl flask into a 200 cc. volumetric flask. When most of the residue has been washed out, wash the flask with 10 cc. of the hot ammonium acetate (d) and again with water. Now add 10 cc. of nitric acid to the volumetric flask. Make to the mark and shake well. Allow the sample to settle out or filter a portion of it. Pipet 40 cc. into a 125 cc. separatory funnel, add 2 cc. of ammonium thiocyanate solution (a), mix, and add 15 cc. of ether. Shake well and allow the ether layer to separate out. (If large quantities of iron are present two or even three extractions may be necessary.) Draw off the bottom layer, which should be nearly colorless, into a beaker, and after adding 25 cc. of reagent (i), transfer the solution to the Nessler tube of the colorimeter and make to mark. Mix with four or five gentle strokes of a plunger and place the tube in position in the colorimeter. After the light in the colorimeter has been turned on at least 1 minute, adjust the rheostat so that the micro-ampere reading is 100. Now add four drops of the sodium sulfide (h), mix with three gentle strokes of the plunger, and take the micro-ampere reading at once. (If the tube is allowed to stand the reading will fall slowly, thus giving results that are too high.) The reading obtained, when referred to a graph prepared with known quantities of lead under similar conditions, gives the quantity of lead present.

#### DISCUSSION

The photo-electric colorimeter method is free from the faults of the usual colorimetric or nephelometric methods. It gives accurate and consistent results, and is also rapid. Some of the advantages are listed.

(1) As the output of the photo-cell is read on a microammeter, the readings of which correspond to definite quantities of lead, personal errors are eliminated.

<sup>1</sup> *This Journal*, 16, 76 (1933), also 1933 report of Associate Referee.

(2) Foreign matter present or a considerable turbidity before precipitation of lead does not interfere, as this can be easily corrected for by an increase of voltage. It must be noted, however, that such a correction cannot be made if a color is present in the solution, because any particular color retards only a portion of the light waves to which the photo-cell is sensitive. Colors, however, are seldom, if ever, present as all organic matter has previously been destroyed by digestion. The fact that considerable turbidity does not interfere is an important advantage of the method, as this makes it possible to determine lead on apple pomace, cabbage, celery, etc. when there are present large quantities of calcium that would interfere with other colorimetric methods.

(3) The reading of the lead sulfide can be made very quickly, before it has an opportunity to coagulate. Experimentally the time required to read after the precipitation of the sulfide is 15 seconds or less. This not only represents a saving in time, but for the number of sulfides that precipitate slowly (cadmium, manganese, and zinc) it allows the determination of lead to be made before interference is encountered from this source.

(4) It is not necessary to run standards with the sample. After a graph of standards is made, it is only necessary to check it occasionally to see that the characteristics of the instrument have not changed. However, even this is scarcely necessary as the output of the photo-cell is adjusted to 100 micro-amperes before the precipitation of lead, and thus care is taken of any change in the voltage of the battery, weakening or changing of position of the light bulb, the use of unmatched Nessler tubes, or the filling of the Nessler tube above or below the mark.

(5) Phosphates and calcium do not interfere. The only common metals that interfere are tin, bismuth and mercury. The interference of tin can be overcome by the addition of 1 cc. of concentrated potassium hydroxide solution before the addition of the sodium sulfide. No study has been made of the interference of the rare metals.

It will be noticed that no regard has been paid to the voltage used, this being unnecessary in determinations of lead. The instrument was constructed to read voltage, however, because this would probably be necessary in other photo-electric methods.

## CONCLUSION

More than 2,500 samples of apples have been run by the Division of Chemistry by this method, and it has proved to be very satisfactory. After the arsenic determination has been made one man can determine lead on 10 samples in less than 1 hour. The agreement between samples when known quantities of lead were run was better than 0.001 grain



(0.06 mg.). When regular samples of apples were repeated, in only a few cases was the variation between samples as much as 0.002 grain (0.13 mg). The instrument is sensitive to 0.0002 grain (0.013 mg.) of lead when the whole sample is used. The method has also been used by the National Fruit Products Company, Winchester, Virginia, for determining lead on apple pomace, jelly, vinegar, etc., with excellent results.

## FIRST DAY

### MONDAY—MORNING SESSION

The 3rd Wiley Memorial Address was delivered by Dr. Alfred R. L. Dohme on the subject, "The History and Value of Germicides." The address was published in *This Journal*, 17, 19 (1934).

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### REPORT ON INSECTICIDES, FUNGICIDES, AND CAUSTIC POISONS

By J. J. T. GRAHAM (Insecticide Control, Food and Drug Administration, Washington, D. C.), *Referee*

The collaborative work for 1933 was a further study of the Donovan electrolytic method for the simultaneous determination of lead oxide and copper in Bordeaux-lead arsenate mixtures, which was adopted last year as official, first action.

Two samples of Bordeaux-lead arsenate were selected. Sample 1 was prepared by the Referee from high-grade materials. The content of lead oxide and copper, calculated from a careful analysis of the Bordeaux mixture and lead arsenate used in its preparation, was 15.96 and 8.95 per cent, respectively. Sample 2 was a commercial product that was considered to be representative of this type of material.

The collaborators were requested to make determinations of lead oxide and copper by Method I, which is described in *Methods of Analysis*, A.O.A.C., 1930, p. 39; 1925, pp. 51 and 52, and by Method II, which is given in *This Journal*, 15, 289-292 (1932); 16, 69 (1933).

The collaborative results are shown in the table.

An examination of the table shows that there is good agreement among the results by all the analysts. The results by Method II are in good agreement with those by Method I, and in the case of Sample 1, whose theoretical content of lead oxide and copper was known, the results by both methods check the theoretical values.

Analyses of Bordeaux-lead arsenate can be completed by Method II in about 24 hours, which is much less time than is required by Method I. In Method I there is a possibility of loss of sample during the several filtrations unless care is exercised. In contrast to this, no filtrations are necessary in an analysis by Method II, and it is rapid, accurate, and very satisfactory.

TABLE 1.—*Collaborative results—Bordeaux mixture with lead arsenate*

ANALYST	LEAD OXIDE				COPPER			
	SAMPLE 1		SAMPLE 2		SAMPLE 1		SAMPLE 2	
	METHOD I	METHOD II	METHOD I	METHOD II	METHOD I	METHOD II	METHOD I	METHOD II
	per cent	per cent	per cent	per cent	per cent	per cent	per cent	per cent
A. Alter	16.02	16.03	10.13	10.02	8.89	9.00	10.58	10.60
New York	—	—	10.16	10.10	8.93	8.99	10.59	10.63
Av.	16.02	16.03	10.15	10.06	8.91	9.00	10.59	10.62
J. C. Bubb	15.96	16.03	10.08	9.97	—	8.75	—	10.60
New York	15.99	16.02	10.13	10.01	—	8.87	—	—
Av.	15.98	16.03	10.11	9.99	—	8.81	—	10.60
C. G. Donovan	15.86	15.97	10.00	10.06	8.99	8.97	10.75	10.63
Washington	15.94	16.01	9.96	10.08	9.05	8.88	10.78	10.59
Av.	15.90	15.99	9.98	10.07	9.02	8.93	10.77	10.61
J. P. Henry	15.93	16.05	9.97	10.15	9.00	8.80	10.50	10.55
Washington	15.90	15.94	10.05	10.05	8.91	8.90	10.65	10.60
Av.	15.92	15.99	10.01	10.10	8.96	8.85	10.58	10.58
W. L. Miller	15.77	16.01	9.96	10.19	8.88	8.85	10.55	10.53
New York	15.67	16.01	9.94	10.15	—	8.88	10.62	10.55
Av.	15.72	16.01	9.95	10.17	8.88	8.87	10.59	10.54
M. Sabowitz	15.93	16.06	10.10	10.16	8.78	8.93	10.49	10.60
New York	15.92	16.12	10.10	10.14	8.86	8.88	10.51	10.61
Av.	15.93	16.09	10.10	10.15	8.82	8.91	10.50	10.61
General Av.	15.90	16.02	10.05	10.09	8.92	8.89	10.60	10.59
Av. deviation from mean	.07	.03	.07	.06	.06	.06	.08	.03

## RECOMMENDATIONS

It is recommended that Method II for the determination of lead oxide and copper in Bordeaux-lead arsenate mixtures be adopted as an official method, final action.

## REPORT ON FLUORINE COMPOUNDS

By G. A. SHUEY (University of Tennessee Agricultural Experiment Station, Knoxville, Tenn.), *Associate Referee*

In accordance with the recommendation approved last year,<sup>1</sup> a collaborative study of the method developed by H. H. Willard and O. B. Winter<sup>2</sup> was made during the year. The study included a modification suggested by W. D. Armstrong<sup>3</sup> with respect to the indicator to be used.

The method is based on the principle that fluoride solutions can be titrated with standard thorium nitrate solution when zirconium-alizarin, or alizarin, is used as the indicator. Any interfering elements may be eliminated from the solution to be titrated by volatilizing the fluorine as hydrofluosilicic acid. The method follows:

## REAGENTS

(a) *Zirconium nitrate*.—Dissolve 1 gram of  $\text{Zr}(\text{NO}_3)_4 \cdot 5\text{H}_2\text{O}$  in 250 cc. of water. Preserve as stock solution.

(b) *Sodium alizarin sulfonate*.—Add 1 gram of  $\text{NaC}_{14}\text{H}_5\text{O}_2(\text{OH})_2\text{SO}_3 \cdot \text{H}_2\text{O}$  to 100 cc. of 95 per cent ethyl alcohol, and shake at intervals for several hours. Filter off the residue and dilute the filtrate to 250 cc. with alcohol. Preserve as stock solution.

(c) *Zirconium alizarin indicator*.—Mix 3 cc. of reagent (a) and 2 cc. of reagent (b). Prepare fresh indicator as needed each day.

(d) *Sodium alizarin sulfonate, aqueous solution*.—Add 0.1 gram of  $\text{NaC}_{14}\text{H}_5\text{O}_2(\text{OH})_2\text{SO}_3 \cdot \text{H}_2\text{O}$  to 200 cc. of water, shake at intervals for several hours, and filter.

(e) *Sodium fluoride solutions*.—0.1 *N* and 0.01 *N*. Use purified salt.

(f) *Perchloric acid*.—60 per cent.

(g) *Quartz*.—About 80 mesh.

(h) *Glass beads*.

(i) *Standard thorium nitrate*.—Approximately 0.01 *N*. Dissolve 1.7408 grams of crystallized  $\text{Th}(\text{NO}_3)_4 \cdot 12\text{H}_2\text{O}$  in about 500 cc. of water and dilute to 1000 cc. Standardize by one of the following methods:

(1) Dilute 10 cc. of 0.1 *N* sodium fluoride to exactly 100 cc. Transfer an aliquot of 10 cc. (containing 1.9 mg. of F) to a narrow, tall-form beaker of 100 cc. capacity; add 3 drops of zirconium-alizarin indicator and 10 cc. of neutral 95 per cent ethyl alcohol. Add dropwise (2 drops are usually enough) hydrochloric acid (1+50) to discharge the pink color. Titrate with thorium nitrate to a reappearance of pink color. (The titration should be performed in good light and over a white surface. The pink color develops slowly as the end point is approached.) Correct for the amount of fluorine that combines with the zirconium of the indicator as follows: Place 10 cc. of water, an equal volume of alcohol, and 3 drops of indicator in a beaker and titrate with 0.01 *N* sodium fluoride to disappearance of pink color. Add to each reading the amount of fluorine required to decolorize 3 drops of indicator. (This correction must be applied when 3 drops of indicator are used. A specific correction is required for each variation in the amount of indicator.) Record value of thorium nitrate in terms of mg. equivalent of fluorine per cc.

(2) Dilute 10 cc. of 0.1 *N* sodium fluoride to exactly 100 cc. Transfer an aliquot of 10 cc. to a narrow, tall-form beaker of 100 cc. capacity; add 3 drops of alizarin

<sup>1</sup> *This Journal*, 16, 153 (1933).

<sup>2</sup> *Ibid.*, 105; *Ind. Eng. Chem. Anal. Ed.*, 5, 7 (1933).

<sup>3</sup> *J. Am. Chem. Soc.*, 55, 1741 (1933).

indicator, reagent (d), and 10 cc. of neutral 95 per cent alcohol. If the solution is not yellow after the addition of the indicator, add dropwise hydrochloric acid (1+50) until the yellow color appears and then add one drop in excess. Titrate to a faint permanent pink with thorium nitrate. According to Armstrong,<sup>1</sup> "The solution shades from yellow to pink as the end point is approached, and the use of a reference solution of the lake with a slight pink color makes for more accurate results." From the buret reading, subtract the amount of thorium nitrate required to form a slight pink color (lake) with three drops of the indicator. Calculate the value of thorium nitrate in terms of fluorine.

#### DETERMINATION

##### *Method I.—Water-soluble Fluorides (interfering elements absent)*

Dissolve about 50 mg. of the salt in water and dilute to 100 cc. Transfer an aliquot of 10 cc. to a small tall-form titrating beaker (a 7×7/8 in. test tube serves well), and add 3 drops of indicator and 10 cc. of neutral 95 per cent alcohol. Add several drops of HCl (1+50) to discharge the pink color. Titrate with 0.01 *N* thorium nitrate to a reappearance of pink color. Correct for the amount of fluorine that combines with the zirconium of the indicator. If alizarin, reagent (d), is used, correct for the amount of thorium nitrate required to form a lake, as previously directed.

##### *Method II.—Water-insoluble Fluorides (interfering elements present,<sup>2</sup> organic matter absent)*

Place into a 100 cc. Pyrex distillation flask a quantity of the sample equal to 18–24 mg. of fluorine, drop in 6 glass beads and about 0.05 gram of 80-mesh quartz, and then add 10 cc. of water and 5 cc. of 60 per cent perchloric acid. Support the flask on an asbestos mat having a circular opening sufficiently large to expose the lower third of the flask to the flame. Close the flask with a 2-holed rubber stopper through which passes a thermometer and a capillary tube, both of which should extend down into the liquid. Connect a 50 cc. dropping funnel with the capillary tube, so that water may be added during the distillation, and connect the side-neck of the distilling flask with a Liebig condenser. Collect the distillate in a 200 cc. Erlenmeyer flask through a short-stemmed funnel. Heat slowly until the initial boiling point of 110°–112° C. is reached. Continue the distillation until the boiling point reaches 135° and hold at approximately that temperature, by allowing water to enter slowly from the dropping funnel, until the distillate measures 75–80 cc. Make the solution alkaline to phenolphthalein with 5 per cent NaOH, evaporate to 50 cc., cool, and render just acid with dilute HCl. Transfer to a 100 cc. volumetric flask and make up to mark with water. Transfer a 10 cc. aliquot to a titrating beaker; add 3 drops of zirconium-alizarin, or alizarin, indicator; restore the pink color by adding, dropwise, 1 per cent NaOH, and then add 10 cc. of 95 per cent alcohol and several drops of HCl (1+50) to discharge the color. Titrate with 0.01 *N* thorium nitrate to a reappearance of pink color. Correct as usual for indicator.

##### *Method III.—Fluorine (organic matter present)*

Weigh 5 grams of the finely-divided material into a 50 cc. platinum dish, and add 5 cc. of freshly prepared  $\text{Ca}(\text{OH})_2$  suspension. Stir with a small glass rod, and add small quantities of water until the entire charge is thoroughly moistened and

<sup>1</sup> *Loc. cit.*

<sup>2</sup> *Notes.*—Ions (e.g.  $\text{Ca}^{++}$ ,  $\text{Ba}^{++}$ ,  $\text{Fe}^{+++}$ ,  $\text{Al}^{+++}$ ,  $\text{PO}_4^{--}$ , etc.) that form a precipitate or nondissociated salt with fluorine or with thorium interfere with the direct titration and must be separated from the solution to be titrated. (Titration of the unknown should be made in approximately the same volume, with the same amount of indicator as that employed in standardising the thorium nitrate, and to the same delicate pink.)

intimately mixed, and then dry in a hot air oven. Ignite gently over a flame until the charge is just charred and complete the ignition in a muffle furnace heated to dull redness. (It may require 24–30 hours for thorough ignition at this temperature.) Transfer the ash to a 100 cc. Pyrex distillation flask, and proceed as directed in Method II, except to use 10 cc. of 60 per cent perchloric acid.

#### COLLABORATIVE STUDY

Six samples were chosen for this study. Sample 1 was prepared from Baker's C. P. sodium fluoride and contained 45.24 per cent fluorine. Collaborators were instructed to use this salt for standardizing thorium nitrate solutions. Sample 2 was pure sodium fluoride diluted with sodium sulfate and contained 42.25 per cent fluorine. Sample 3 was pure sodium fluosilicate with a theoretical fluorine content of 60.54 per cent. Sample 4 was barium fluosilicate with an unknown fluorine content. Sample 5 was cryolite (Kryolith) furnished by courtesy of F. J. Frere, Pennsylvania Salt Manufacturing Co., who reported a fluorine content of 54.06 per cent. Sample 6 was fluospar, U. S. Bureau of Standards sample No. 79, and contained 94.9 per cent  $\text{CaF}_2$ , or 46.02 per cent of fluorine.

D. S. Reynolds, U. S. Department of Agriculture, Bureau of Chemistry and Soils; W. D. Armstrong, University of Minnesota, and the Associate Referee collaborated in the work.

Samples were furnished to each collaborator, with directions for preparing reagents and making the determinations. Collaborators were instructed to analyze Samples 2 and 3 according to Method I, and to use three separate indicators. Results are given in Table 1.

On Sample 2, 31 results are reported for the three indicators. The average weight of sample contained in a 10 cc. aliquot (the volume titrated in each case) was 4.4 mg. This weight of sample carried 1.859 mg. of fluorine, and required, for titration, an average of 9.95 cc. of 0.01 *N* thorium nitrate.

Collaborators reported 32 results on Sample 3. The average weight of sample per 10 cc. aliquot was 4.46 mg.; it had a fluorine content of 2.704 mg. and required an average of 13.95 cc. of 0.01 *N* thorium nitrate.

The average of results reported for Sample 2 by Collaborators B and C, using indicator 1, is 0.87 per cent lower than the average result reported by Collaborator A, for the same indicator. Collaborators B and C report 0.38 per cent below Collaborator A for indicator 2. For indicator 3, the average of all results agree within 0.23 per cent.

The averages found for Sample 2 by all collaborators using indicators 1, 2, and 3, are 41.86, 42.43, and 42.33 per cent fluorine, respectively. The averages found in the same sample by each collaborator, with the three indicators, are A, 42.54; B, 41.97; and C, 41.99. The average of all results on Sample 2 is within 0.05 per cent of the theoretical amount of fluorine present in the sample.

TABLE 1.—Fluorine content of water-soluble fluorides (Method I)

SAMPLE NUMBER	COLLABORATOR A			COLLABORATOR B			COLLABORATOR C			AVERAGE FLUORINE FOUND	FLUORINE RECOVERED	FLUORINE PERCENT
	1*	2*	3*	1	2		1	2	3			
2	per cent	per cent	per cent	per cent	per cent		per cent	per cent	per cent	per cent	per cent	per cent
	42.37	42.67	42.34	41.47	42.33		41.52	42.11	42.23			
	42.46	42.58	42.52	41.70	42.40		41.63	42.24	42.19			
	42.46	42.75	42.52	41.47	42.40		41.59	42.16	42.26			
Av.	42.50	43.01	42.43	41.62	41.54		41.54	42.24	42.19			
	42.44	42.75	42.45	41.57	42.37		41.57	42.18	42.22		98.88	42.24
3	60.47	60.36	60.26	60.59	60.67		60.53	60.52	60.54			
	60.47	60.64	60.35	60.59	60.59		60.56	60.52	60.49			
	60.43	60.26	60.57	60.49	60.71		60.56	60.54	60.54			
	60.35	60.52	60.48	60.45	60.63		60.53	60.55	60.52			
Av.	60.43	60.44	60.41	60.53	60.65		60.54	60.53	60.52		99.93	60.54

\* Indicator 1 is titanium-alizarin, reagent (c); 2 is alizarin (sodium alizarin sulfonate), reagent (d); and 3 is titanium-alizarin prepared according to Reynolds; i.e. dissolve 1 gram of sodium alizarin sulfonate in 100 cc. of water, filter, and add 150 cc. of neutral 95% alcohol. Then add 1 cc. of this alizarin to 3 cc. of titanium, reagent (a).

The results reported for Sample 3, for each of the indicators, are in close agreement. The average of all results for this sample is within 0.04 per cent of the amount of fluorine present. It would appear, therefore, that discrepancies shown in the results for Sample 2 could not be attributed to the indicators used. Any of the three indicators will serve; other conditions being equal, the one chosen will probably be a matter of personal preference.

As shown in Table 2, concordant results were obtained for Sample 4. Average recoveries of the fluorine present were for Samples 5 and 6, 98.87 and 99.70 per cent, respectively. Sample 3 was water-soluble and was used to determine the accuracy of the method. As indicated in Table 1, results obtained by direct titration on this sample are accurate. Fluorine was also recovered quantitatively from Sample 3 by distillation. While results of the several collaborators are slightly at variance, the average fluorine recovery was 99.04 per cent.

TABLE 2.—*Fluorine content of water-insoluble fluorides—interfering elements present, organic matter absent (Method II)*

SAMPLE NUMBER	COLLABORATORS			FLUORINE FOUND AVERAGE	FLUORINE RECOVERED AVERAGE	FLUORINE PRESENT
	A	B	C			
	<i>per cent</i>	<i>per cent</i>	<i>per cent</i>	<i>per cent</i>	<i>per cent</i>	<i>per cent</i>
3	60.04	59.80	60.36			
	60.16	59.93	60.34			
	59.36	59.89	60.30			
	59.62		60.33			
Av.	59.67	59.87	60.33	59.96	99.04	60.54
4	35.22	35.33	35.39			
	35.18	35.25	35.34			
	35.37	35.25	35.26			
	35.37		35.40			
Av.	35.28	35.27	35.34	35.29		Unknown
5	53.07	52.89	54.36			
	52.99	52.97	54.26			
	53.23	52.97	54.41			
	53.31		54.30			
Av.	53.15	52.88	54.33	53.45	98.87	54.06
6	45.98	45.21	46.12			
	45.98	45.24	46.22			
	46.15	45.33	46.16			
	46.23		46.14			
Av.	46.08	45.26	46.16	45.80	99.74	46.02



## WATER-INSOLUBLE FLUORIDES, INVOLVING LARGE QUANTITIES OF FLUORINE

To study the accuracy of the method when larger quantities of fluorine are involved, the distillate obtained from 50 mg. of Sample 5 was concentrated to about 25 cc., and an equal volume of alcohol and 3 drops of zirconium-alizarin were added. The whole mixture was then titrated with 0.1 *N* thorium nitrate. Results are shown in Table 3. Difficulty is encountered in titrating fluorine in this concentration with 0.1 *N* thorium nitrate as thorium fluoride imparts to the solution a murkiness that renders detection of the end point very difficult. This fact probably accounts for the high results obtained.

TABLE 3.—*Fluorine content of a water-soluble fluoride (Sample 5)*

SAMPLE OF WEIGHT	COLLABORATORS			FLUORINE FOUND AVERAGE	FLUORINE RECOVERED AVERAGE	FLUORINE PRESENT
	A	B	C			
mg.	per cent	per cent	per cent	per cent	per cent	per cent
50*	54.13 55.25	55.08	54.30 54.46 54.32			
Av.	54.69	55.08	54.36	54.38	100.59	54.06
500†	49.00 49.84	48.30 48.38 48.30	49.38 49.57 49.95			
Av.	49.42	48.33	49.63	49.13	90.86	54.06

\* Determined by titrating the whole of the fluorine obtained from 50 mg. of sample with 0.1 *N* thorium nitrate.

† Determined by titrating 10 cc. aliquots of a 500 mg. charge with 0.1 *N* thorium nitrate.

Charges of 500 mg. of Sample 5 were distilled until 125 cc. of distillate was collected. The distillate was rendered alkaline, evaporated to about 50 cc., acidified, and diluted to 100 cc. Aliquots of 10 cc. were titrated with 0.1 *N* thorium nitrate, zirconium-alizarin being used as indicator. Results of the several collaborators are low and inconsistent, as shown in Table 3. It might at first appear that insufficient distillate was collected to recover all the fluorine. This, however, proved not to be the case. The Associate Referee ran several experiments in which 10 cc. of perchloric acid was used, and 175 cc. of distillate was collected from a 500 mg. charge. The recovery of fluorine was only 92.3 per cent. The large amount of insoluble thorium fluoride proved troublesome in determining the end point of the interaction. As suggested by one of the collaborators, Armstrong, "this difficulty may be due to adsorption of the lake by the insoluble thorium fluoride."

Collaborators were furnished organic material in the form of dried, ground peach leaves, with instructions to use a 5 gram charge, to add 50 mg. of pure sodium fluoride (salt No. 1), and 5 cc. of  $\text{Ca}(\text{OH})_2$  suspension, to proceed according to Method III, and then to repeat, using 50 mg. of Sample 5. The results obtained are given in Table 4.

TABLE 4.—*Fluorine—organic matter present (Method III)*

SAMPLE NUMBER	COLLABORATOR			FLUORINE FOUND AVERAGE	FLUORINE RECOVERED AVERAGE	FLUORINE PRESENT per cent
	A	B	C			
	<i>per cent</i>	<i>per cent</i>	<i>per cent</i>	<i>per cent</i>	<i>per cent</i>	<i>per cent</i>
1	44.03	43.61	44.53			
	44.05	44.24*	44.60			
	44.04	43.92	44.56	44.17	97.62	45.24
5	52.04	51.70	52.94			
	52.11	51.83*	52.80			
	52.07	51.76	52.87	52.23	96.61	54.06

\* 0.05% alizarin indicator used.

For Samples 1 and 5 the average recoveries from the ashed material by all collaborators are 97.62 and 96.61 per cent, respectively.

#### COMMENTS OF COLLABORATORS

A.—I have found that the thorium nitrate solutions should be standardized against the same concentration of fluorine that is found in the average titration. The standard will vary with different concentrations of fluorine.

Titration of large amounts of fluorine with 0.1 *N* thorium nitrate does not give good results. The end point is not so sharp as in more dilute solutions and I believe that better results can be obtained by keeping the amount of fluorine below 5–10 mg.

The distillation of large quantities of fluorine salts is entirely unsuitable, as silica separates out in the condenser and in the distillate when the solution is concentrated.

Low results were obtained when the fluoride was ignited in the presence of plant material, probably due to a volatilization of the fluorine. This might be preventable if the material contained no water, but as large quantities are added in the form of lime water, I do not see any way to prevent this loss.

Taken as a whole, the method gives good results. The titrations check to within 0.01 and sometimes 0.001 mg. of fluorine.

B.—I found that the end point of the titration could be more easily recognized and that more consistent results could be obtained if a solution in which the end-point had been reached were used for comparison. This statement applies to any of the indicators used.

I found the acidity of the hydrofluosilicic containing distillates was difficult to adjust using litmus paper as an indicator. For this reason I used one drop of phenolphthalein, and I suggest that this indicator be substituted for the litmus paper. The

solutions to be titrated are always rendered acid and this substance can introduce no error in the titrations.

While any decision as to the choice of indicators must be determined by the accuracy of the results obtained with each, I prefer, everything else being equal, the aqueous alizarin indicator. The use of the zirconium in the indicator solution unnecessarily complicates the process. The measurement of the zirconium-alizarin indicator by drops allows a considerable chance for error, which could be reduced by measurement of the indicator with a capillary pipet similar to the 0.1 cc. Folin blood pipet. I have observed that the zirconium-alizarin indicator prepared as directed in the foot note of Table 1 gives an end point more easily detected than that prepared according to the original directions. Because the modified zirconium-alizarin indicator contains a higher concentration of sodium alizarin sulfonate than the original indicator, it appears that the better end point is due to the higher concentration of the dye. It seems probable that the color reached at the end point with the zirconium-alizarin indicator is that of the thorium lake and is not due to the reconversion of the zirconium to its lake. In this case the zirconium serves no function. However, the indicator of choice is the one which gives the most accurate results.

### CONCLUSIONS

The Willard-Winter method is accurate for the direct titration of pure fluoride solutions in small quantities. Fluorine can be recovered quantitatively by distillation with perchloric acid from water-soluble and insoluble fluorides. Titrations are not accurate in the presence of large quantities of thorium fluoride. The choice of indicators is a matter of preference. The recovery of fluorine from plant ash is incomplete, and this factor should be studied further.

### RECOMMENDATIONS<sup>1</sup>

It is recommended—

(1) That the modification of the Willard-Winter method for the determination of fluorine in fluorine compounds presented in this report be adopted as a tentative method.

(2) That further study be conducted with respect to the recovery of fluorine from plant ash.

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## REPORT ON SUGAR AND SUGAR PRODUCTS

By J. A. AMBLER (Bureau of Chemistry and Soils, U. S. Department of Agriculture, Washington, D. C.), *Referee*

The work done during the past year on the analysis of sugars and sugar products will be presented and discussed in detail by the Associate Referees on Honey, on Maple Products, on Drying, Densimetric and Refrac-

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<sup>1</sup> For report of Subcommittee A and action of the Association, see *This Journal*, 17, 45 (1934).

tometric Methods, on Polariscopic Methods, and on Chemical Methods for Reducing Sugars, whose reports will follow. The recommendations for further study advanced by these associate referees are approved by the Referee.

The attention of the Referee has been called to the fact that the tentative method for the determination of diastase in honey given in *Methods of Analysis*, A.O.A.C., 1930, is out of date and that a newer and better method is desirable. It is therefore suggested that the method of Gothe be studied with the idea of improving it as much as possible in order to present it to the Association for inclusion in the next revision of methods.

No report on honey was given by the associate referee.

### REPORT ON MAPLE PRODUCTS\*

By J. F. SNELL (Macdonald College, Province of Quebec, Canada),  
*Associate Referee*

The year's work on maple products was designed to embrace a comparison of densimetric and refractometric methods for total solids and further work on lead values with special reference to the reagent made from activated litharge.<sup>1</sup>

Table 1 gives the names and addresses of the collaborators, Table 2 the description of the pure sirups donated, as last year, by the Quebec De-

TABLE 1.—*Collaborators on maple products, 1933*

REFERENCE LETTER	LABORATORY	ADDRESS	DIRECTOR	ANALYST
F	Macdonald College	Macdonald College, P.Q., Canada	J. F. Snell	G. H. Findlay
Ho	"	"	"	R. Holcomb
B	Chem. & Tech. Res., U. S. Bur. Chem. & Soils	Washington, D.C.	C. A. Browne	S. Byall
J	Dom. Exptl. Farms System	Ottawa, Canada	F. T. Shutt	A. C. Medcalf
H	Acadia University	Wolfville, N.S.	D. U. Hill	G. T. Eaton
C	American Tobacco Co.	Richmond, Va.	H. R. Hanmer	O. N. Coty and O. L. Hillsman

\* Contribution from the Faculty of Agriculture of McGill University, Macdonald College, P. Q., Canada. Journal Series No. 46.

<sup>1</sup> *This Journal*, 16, 168 (1933).

TABLE 2.—*Pure maple sirups examined collaboratively, 1933*

NO.	ADDRESS	COUNTY	RUN	COLOR	TOTAL SOLIDS	REMARKS
					<i>per cent</i>	
1	Ste. Lucie	Montmagny	Middle	Light	67.20	
3	" "	"	Early	Dark	69.25	
5	" "	"	Middle	Dark	68.33	
6	St. Adalbert	L'Islet	Middle	Medium	67.75	
A	" "	"	Early	Medium	68.00	
8	" "	"	Last	Dark	66.60	Fermented
9	Ste. Perpetue	L'Islet	Middle	Dark	62.30	
10	" "	"	Middle	Medium	64.10	
B	" "	"	Last	Dark	60.75	
12	St. Pamphile	L'Islet	Early	Medium	64.90	
13	" "	"	Middle	Medium	68.90	
15	" "	"	Last	Dark	65.44	
17	Winslow	Frontenac	Middle	Medium	68.90	
C	" "	"	Middle	Light	66.70	
18	" "	"	Early	Dark	65.65	
21	" "	"	Last	Dark	68.27	
22	St. Sylvestre	Lotbiniere	Middle	Medium	64.47	
23	" "	"	Middle	Medium	64.10	Fermented
25	" "	"	Last	Dark	67.35	
26	St. Victor	Beauce	Middle	Dark	67.17	
27	Composite of	A, 1, 6, 10		Medium	67.15	
28	" "	B, 3, 5, 15, 17		Medium	66.95	
30	" "	C, 9, 21, 22, 25		Dark	63.60	

partment of Agriculture, and Table 3 the description of the adulterated samples. To provide for the densimetric work larger samples than in previous years had to be sent to the collaborators, and it was found necessary to combine the whole of the sirups A, B and C with smaller portions of other sirups to make samples 27, 28 and 30, which were then used to make the adulterated sirups of Table 3 by admixture of a sirup made from refined sugar.

#### TOTAL SOLIDS

Refractometric results on total solids in the sirups as received were reported by 6, densimetric results by 5, analysts. Collaborators were instructed to check the setting of their refractometers with standard plates or with liquids of standard purity—nitrobenzene  $n_D^{20} = 1.5548$ , methyl salicylate  $n_D^{20} = 1.5395$  or benzyl benzoate  $n_D^{20} = 1.5705$ —and to adjust them if out by more than 0.0005. The danger of the deposition of dew on the prisms was pointed out and circulation of water of room temperature through the jackets was recommended as a preventive precaution. Careful cleansing and drying of the embedding cement as well as of the prisms themselves were prescribed.

TABLE 3.—*Adulterated sirups examined collaboratively, 1933*

NO.	COMPOSITION		TOTAL SOLIDS
	per cent	per cent	per cent
2	80 No. 27+20 S		66.72
4	65 No. 27+25 S		66.50
7	50 No. 27+50 S		66.37
11	80 No. 28+20 S		66.76
14	65 No. 28+35 S		66.40
16	50 No. 28+50 S		66.35
19	80 No. 30+20 S		63.85
20	65 No. 30+35 S		64.30
24	50 No. 30+50 S		64.65
26	35 No. 30+65 S		64.95

Collaborator C found it necessary to make his measurements at the high laboratory temperature of 39° and used tap-water of 29° for the prism jackets. He reports that no deposition of dew was observed. In his laboratory the refractometer readings made by one analyst were checked by a second and, in case of disagreement, by a third, analyst. In 16 out of the 30 sirups, the refractometric results of this collaborator were the lowest reported. In 16 of the 30, collaborator J reported minimum results (coincident in 3 instances with those of C). In a single instance the lowest result reported was that by H. Maximum results were well distributed, F having 11, Ho 10 (1 coincident with F), B 1 and H 9. If the results of analysts C and J were ignored, as well as the single low result of H, the results would be in still better agreement than those obtained last year, the range among the remaining analysts varying in the 30 sirups from 0.10 to 1.29 per cent total solids and being in only two instances (0.92 and 1.29) greater than 0.73. On the other hand, when all the reports are included, the lowest range found is 1.0, the highest 1.76 and the average 1.42 per cent.

In the densimetric determinations, made with Brix spindles, collaborators F and H obtained in general low, and collaborator C in general high, results as compared with the others. F had the minimum report on 13 of the samples, H on 16, while Ho and B coincided in the minimum on the remaining one of the 30 sirups. On the other hand C's report was the maximum in no less than 22 of the sirups, Ho's in 8, B's in 3 and F's in 1 (there being 1 instance of three and 3 of two collaborators coinciding in maximum reports).

Table 4 gives the average of the total solids reported by each collaborator for the 30 sirups and the number of samples upon which each obtained the highest and lowest results reported. It is evident that better agreement among the five collaborators who used both methods was reached by the densimetric than by the refractometric method, though for the

TABLE 4.—*Total solids. Average of results of each collaborator on the 30 sirups*

COLLABORATORS	F	HO	B	J	H	C	RANGE	RANGE OMITTING J AND C
Average per cent:								
Refractometric	66.07	66.0	65.9	64.9	66.17	64.9	1.42	0.43
Densimetric	66.18	66.51	66.46	—	66.32	66.66	0.70	0.53
Difference	0.11	0.51	0.56	—	0.15	1.76	—	—
Number of minimum reports:								
Refractometric	0	0	0	16	1	16	—	—
Densimetric	13	1	1	—	16	0	—	—
Number of maximum reports:								
Refractometric	11	10	1	0	9	0	—	—
Densimetric	1	8	4	—	0	22	—	—
Variation between methods <sup>1</sup>	0.37	0.52	0.58	—	0.22	1.74	—	—

<sup>1</sup> The arithmetic average of the differences between results on individual sirups.

four analysts, F, Ho, B and H, the agreement was somewhat better for the refractometric than for the densimetric method.

A comparison of the results of each analyst by the two methods shows that the densimetric results of three analysts, Ho, B and C, are all higher than the refractometric, while with F and H there was variation in both directions. The averages given for F and H in the last line of Table 4 are arithmetic averages of the variations in both directions. No densimetric figures were reported by J. It will be noted that for each collaborator the average total solids for the 30 sirups is higher by the densimetric than by the refractometric method. This may be because the tables (and graduations), from which the total solids are derived relate to pure sucrose, and the non-sugars of the sirup have more effect upon the density than upon the refractive power of the sirup.

#### PREPARATION OF SAMPLE

In the preparation of sample for analysis the directions as amended in 1931<sup>1</sup> and 1932<sup>2</sup> were given, but the use of suction or of filter aid was not recommended. Analyst H reported that, working on two days at a relative humidity of 93, he found it necessary to boil to a solids content of 66 per cent or more, as during filtration the sirup became more diluted instead of more concentrated.

By comparison of Table 5 with Table 7 of last year's report<sup>3</sup> it will be seen that analysts F and J obtained results of less range and averaging more closely to 65.0 per cent solids than were obtained last year. Were it

<sup>1</sup> *This Journal*, 15, 179 (1932).

<sup>2</sup> *Ibid.*, 16, 79 (1933).

<sup>3</sup> *This Journal*, 16, 164 (1933);

TABLE 5.—*Refractometric total solids as prepared for analysis—after filtration but before adjustment*

ANALYST	F	HO	B	J	H	AVERAGE
Average	65.10	65.14	65.64	65.26	65.52	65.33
Maximum	65.45	66.4	68.5	65.7	66.34	
Minimum	64.84	64.0	64.5	64.7	64.14	
Range	0.61	2.4	4.0	1.0	2.20	2.04

not for the one extreme figure of 68.5, B's range would also be narrower than last year (2.3 as compared with 3.1), though his average (65.5) would still be farther from the mark (65.0) than last year (65.32).

The data corresponding to those of Table 8 of last year's report are as follows: Number of analysts 5; number of preparations 146; solids of filtered sirup—general average 65.32; lowest average by an analyst 65.10; highest average by an analyst 65.64; average difference between analysts' maximum and minimum 2.04; maximum range for an analyst 4.0; minimum range for an analyst 0.61; number of analysts preparing all samples within 5 per cent, 5, i.e., all; within 2 per cent, 2; to, or within, 1 per cent, 2.

These results confirm the superiority of the method of refractometric control over that dependent solely on boiling temperature.

For the cooling of the small sample of boiling sirup, analyst Ho replaced the 1 cc. pipet with a piece of glass tubing drawn to a capillary and bent twice at right angles so that it could be set upon a beaker in such a position that the elbow could be cooled in running water while the tip was out of reach of water. Analyst H, having tried this device, regards the 1 cc. pipet as equally satisfactory.

#### CONDUCTIVITY VALUES

Analyst F determined conductivity values. The twenty pure sirups gave values ranging from 145.2 to 204.6 and averaging 177.6. The range of values (59.4) is 33 per cent of the average and 41 per cent of the minimum. The adulterated sirups were found to have conductivity values corresponding to maple contents somewhat above the actual (see Table 10). This accords with results previously reported.

#### CANADIAN LEAD VALUES

All 6 collaborators reported Canadian lead values (Fowler modification), and all but H, Winton lead values, determined with reagents prepared from activated litharge.<sup>1</sup> For comparison three analysts made determinations with solutions prepared from dry lead subacetate. All these reagents were analyzed by the one analyst, F.

The Canadian values obtained with the activated litharge reagents are summarized in Table 6, and those with the dry basic acetate reagents in

<sup>1</sup> *This Journal*, 16, 80 (1933).



TABLE 6.—*Canadian lead values with activated litharge reagent—pure sirups*

TABLE 6.—Continuation of data from preceding table														
	ANALYST						MEAN	RANGE	RANGE % OF MEAN	SD†				
	P	HO	B	J	E	G								
No. of sirups	20	17	20	20	17	20	4.82	0.33	6.84					
Av. lead values	4.69	4.74	5.02	4.90	4.85	4.70	6.41	1.09*	17.0*					
Max. lead values	6.18	6.07	7.16	6.44	6.39	6.22	2.87	0.30	10.4					
Min. lead values	2.79	2.96	2.80	2.92	3.03	2.73	3.54							
Range	3.39	3.11	4.36	3.52	3.36	3.49	73.3							
Range % Av.	72.3	65.6	86.8	71.8	69.3	74.2	122							
Range % Min.	121.5	105	156	120.5	111	118								
Analysis of reagents														
pH	7.5	7.4	7.5	7.4	7.5	7.5	7.47	0.1	1.3	7.4				
Density	1.252	1.250	1.255	1.250	1.251	1.247	1.251	0.008	0.64	1.250				
Alkalinity	9.59	9.79	10.04	9.98	10.00	9.98	9.90	0.45	4.55	9.99				
Total Pb	.2318	.2297	.2353	.2312	.2322	.2281	.2314	.0072	3.11	.2350				
Neutral Pb	.1324	.1283	.1312	.1278	.1286	.1247	.1288	.0077	5.98	.1315				
Basic Pb	.0994	.1014	.1041	.1034	.1036	.1034	.1025	.0047	4.58	.1035				
Ratio N:B	1.33	1.27	1.26	1.24	1.24	1.21	1.26	0.12	9.52	1.27				

\* Omitting B's maximum, range = 0.37, range % mean = 5.7.

† Used only in the preparation of the reagent for the Winton method.

Table 7. These tables also include the results obtained in the analysis of the reagents. It will be noted that with the activated litharge reagent (1) closer concordance among analysts and (2) higher lead values were realized, but (3) the range of the values in genuine sirups was distinctly greater. Tables 8 and 9, summarizing the experience of five years' collaboration, corroborate this year's evidence on these points.

TABLE 7.—*Canadian lead values with lead subacetate reagent—pure sirups*

	ANALYST			MEAN	RANGE	RANGE PER CENT OF MEAN
	F	HO	B			
No. of sirups	20	17	20			
Av. lead values	4.57	4.61	4.23	4.47	0.38	8.50
Max. lead values	5.91	5.88	5.65	5.81	0.26	4.47
Min. lead values	2.73	2.88	2.59	2.73	0.29	10.6
Range	3.18	3.00	3.06	3.08		
Range % Av.	69.6	65.1	72.4	69.0		
Range % Min.	116	104	118	113		

*Analysis of reagents*

pH	7.3	7.3	7.4	7.33	0.1	1.36
Density	1.251	1.252	1.253	1.252	0.002	0.16
Alkalinity	8.81	9.44	9.80	9.32	0.99	10.6
Total Pb	0.2319	0.2328	0.2292	0.2313	0.0036	1.56
Neutral Pb	0.1406	0.1350	0.1276	0.1344	0.0130	9.66
Basic Pb	0.0913	0.0978	0.1016	0.0969	0.0103	10.6
Ratio N:B	1.54	1.38	1.28	1.40	0.16	11.4

TABLE 8.—*Canadian lead values—concordance among analysts with the two reagents*

YEAR	ACTIVATED LITHARGE REAGENT					DRY SUBACETATE REAGENT				
	NUMBER OF RE- AGENTS*	NUMBER OF SIRUPS	RANGE AMONG ANALYSTS AS PER CENT OF MEAN			NUMBER OF RE- AGENTS*	NUMBER OF SIRUPS	RANGE AMONG ANALYSTS AS PER CENT OF MEAN		
			MIN.	MAX.	AV.			MIN.	MAX.	AV.
1919	—	—	—	—	—	8	20	11	40	20
1930	—	—	—	—	—	4-6	24	9	41	23
1931	9	8	7	27	13	11	8	25	42	31
1932	7	30	5	47	18	—	—	—	—	—
1933	6	17-20	6	23	13	3	17-20	2	30	12

\* The number of reagents is given instead of the number of analysts because in a few instances one analyst used more than one reagent of each class.

As regards the rate of falling off of the lead value with progressive adulteration with refined sugar (Table 10), the activated litharge again shows superiority, the maple content indicated by the ratio of the Canadian lead values of the adulterated sirups to that of the original being

TABLE 9.—*Canadian lead values—range in genuine sirups with the two reagents*

YEAR	ACTIVATED LITHARGE REAGENT				DRY SUBACETATE REAGENT			
	NUMBER OF RE-AGENTS*	NUMBER OF SIRUPS	RANGE AS PER CENT OF		NUMBER OF RE-AGENTS*	NUMBER OF SIRUPS	RANGE AS PER CENT OF	
			AVERAGE VALUE	MINIMUM VALUE			AVERAGE VALUE	MINIMUM VALUE
1929	—	—	—	—	8	20	86	101
1930	—	—	—	—	8	5-24	62	88
1931	9	8	53	77	11	8	49	71
1932	4	30	125	227	1	30	99	166
1933	6	17-20	73	124	3	17-20	69	113

\* See footnote to Table 9!

TABLE 10.—*Effect of adulteration with sucrose*

Comparison of actual maple content with that indicated by Canadian and Winton lead values and by conductivity value

SIRUP NO.	ACTUAL MAPLE CONTENT	MAPLE CONTENT INDICATED BY MEAN				CONDUCTIVITY VALUE
		CANADIAN LEAD VALUE		WINTON LEAD VALUE		
		LITHARGE REAGENT	SUBACETATE REAGENT	LITHARGE REAGENT	SUBACETATE REAGENT	
	<i>per cent</i>	<i>per cent</i>	<i>per cent</i>	<i>per cent</i>	<i>per cent</i>	<i>per cent</i>
27	100	100	100	100	100	100
2	80	76	79	80	79	83
4	65	59	64	65	63	72
7	50	40	44	46	45	57
28	100	100	100	100	100	100
11	80	73	73	78	74	81
14	65	54	55	60	59	68
16	50	35	40	45	46	55
30	100	100	100	100	100	100
19	80	75	78	79	80	84
20	65	58	60	63	63	69
24	50	41	46	47	48	56
29	35	23	29	29	30	40

Actual values in the pure sirups (mean of all analysts' results)

27	100	4.94	4.69	2.25	2.04	180
28	100	3.86	3.62	1.82	1.67	158
30	100	5.90	5.56	2.42	2.20	199

lower than where reagents made from dry basic acetates were used. The figures given in Table 10 for the litharge reagent are the averages of those calculated from the lead values of five (in the case of sirup No. 28, six) analysts, those for the dry basic acetate reagent the average of those of three analysts.

In three of the four series of adulterated sirups analyzed in 1932, also, the activated litharge reagent showed itself somewhat superior in the rate of fall of the value in progressive adulteration.<sup>1</sup>

### WINTON LEAD VALUES

Four collaborators reported Winton values determined with the use of the activated litharge reagent made by diluting that prepared for the Canadian method, and another analyst (Ho) those determined with a reagent similarly prepared from a reagent differing slightly in total lead content and alkalinity from that used by him in the Canadian determinations (see last column of Table 6). Results are given in Table 11, which also includes the Winton lead values of F and B obtained with reagents made by diluting their Canadian reagents made from dry basic lead acetate.

TABLE 11.—*Winton lead values—pure sirups*

	ANALYST					MEAN	RANGE	RANGE PER CENT OF MEAN
	F	HO	B	J	C			
(a) With activated litharge reagent								
No. of sirups	20	20	20	20	20	—	—	—
Av. lead values	2.21	2.12	2.12	2.19	2.07	2.13	0.14	6.57
Max. lead values	2.73	2.76	2.76	2.70	2.67	2.70	0.12	4.45
Min. lead values	1.52	1.52	1.52	1.50	1.38	1.47	0.14	9.52
Range	1.21	1.24	1.24	1.20	1.29	1.23	—	—
Range % Av.	54.8	58.6	58.6	54.8	62.3	57.7	—	—
Range % Min.	79.6	81.6	81.6	80.0	93.4	83.8	—	—
(b) With lead subacetate reagent								
No. of sirups	20	—	20	—	—	—	—	—
Av. lead values	2.11	—	1.73	—	—	1.92	0.38	19.8
Max. lead values	2.59	—	2.07	—	—	2.33	0.52	22.3
Min. lead values	1.47	—	1.31	—	—	1.39	0.16	11.5
Range	1.12	—	0.76	—	—	0.94	—	—
Range % Av.	53.1	—	42.9	—	—	48.0	—	—
Range % Min.	76.2	—	58.0	—	—	67.1	—	—

As in the Canadian method the values obtained with the activated litharge reagents are higher than the others. The agreement among collaborators is distinctly better with the activated litharge reagent, whether it is judged by the tabulated averages or comparison is limited to the results of the two analysts who used both reagents. As in the Canadian values, also, the range of lead values among the genuine sirups is greater for the litharge reagent than for that made from the dry subacetate. In

<sup>1</sup> See Table 12 of 1932 Report, *This Journal*, 16, 170 (1933).

the adulterated sirups (see Table 10) there was no material difference between the two reagents as regards the decrease of lead value with progressive adulteration.

#### SUMMARY

1. For total solids the densimetric gave better concordance among the analysts as a whole than the refractometric method. Omitting the results of one who operated at a temperature of 39°, and those of another who made no densimetric measurements, the refractometric method showed a slight superiority.

2. On the average and in the great majority of individual sirups, the densimetric results are higher than the refractometric.

3. In the preparation of the sample, refractometric control continues to give satisfaction.

4. The advantages of preparing the lead value reagents from activated litharge rather than from dry basic lead acetate are further demonstrated. These are (a) greater uniformity of reagent, (b) better concordance among analysts, (c) higher lead values, both Canadian and Winton, and (d) more rapid decrease of Canadian lead value in progressive adulteration with sucrose.

5. The range of variation of the lead values in genuine sirups is somewhat greater for the activated litharge reagent than for the other. In the Associate Referee's opinion this disadvantage is out-weighed by the advantages mentioned in the preceding paragraph.

#### RECOMMENDATIONS<sup>1</sup>

It is recommended—

(1) That in the tentative method for preparation of maple sirup for analysis [*Methods of Analysis*, A.O.A.C., 1930, p. 391, 103 (a)] the concluding sentence, viz., "To facilitate the filtration a hot water funnel, suction or a 'filter-aid' may be employed" be deleted and that the method as so amended be adopted as official (first action).

(2) That to the official method for determining moisture in maple sirup (p. 391, 104) the following sentence be added: "In the refractometric measurement guard against deposition of dew on the prisms by circulating water of room temperature through the prism jackets and correcting the observations to 20° by use of Table 7, p. 512 (official, final action) if appropriate in view of the addition of the words "of room temperature" to the form adopted as official, first action, last year [*This Journal*, 16, 79 (8)]; otherwise, official (first action).

(3) That the directions for official polarimetric determination of sucrose in maple products, p. 392, 107, be changed to read as follows: "Cal-

<sup>1</sup> For report of Subcommittee A and action of the Association, see *This Journal*, 17, 45 (1934).

culate from the results of 105, using the appropriate formula from 22 or 23" (official, final action).

(4) That the directions for the preparation of reagents for the determination of Winton and Canadian lead values adopted as official (first action) last year [*This Journal*, 16, 80 (10) and (11)], be adopted as official (final action).

(5) That data be accumulated to define the limits of the lead values obtained in the use of these reagents upon genuine maple products.

(6) That the directions for determining conductivity value as revised last year and adopted as official (first action), [*This Journal*, 15, 80-81 (12)], be adopted as official (final action) and substituted for those on pp. 393-4, 120 and 121.

(7) That the changes in the official directions for preparation and use of clarifying reagents adopted last year under Nos. (1), (2), (3) and (4), *This Journal*, 16, 78-9, as official (first action), be adopted as official (final action).

(8) That the amendment to the official refractometric method for the determination of solids, p. 365, 7, adopted as official (first action) last year, [*This Journal*, 16, 81 (13)], be adopted as official (final action).

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## REPORT ON DRYING, DENSIMETRIC, AND REFRACTOMETRIC METHODS

By CARL F. SNYDER (U. S. Bureau of Standards, Washington, D. C.),  
*Associate Referee*

In the official refractometric method for the determination of solids in sugar solutions reference is made to the table of refractive indices of Schönrock. This table gives the indices of sucrose solutions to four decimal places. With the more general use of refractometers for precision measurements it has become necessary that values to five places be made available.

E. Landt<sup>1</sup> reports the results of his measurements on sucrose solutions of concentrations from 0 to 26 grams in 100 cc. of solution. His measurements were made by means of a new immersion refractometer of Zeiss provided with a single prism with a sufficient range for these concentrations. This instrument is of importance in that it permits refractometer measurements on the same normal solutions that are used for the determinations of alkalinity, ash, polarization, etc. Landt also reports the so-called 1933 Schönrock values, which are based on Schönrock's original experimental data recalculated to the fifth decimal place. Agreement between the values of Landt and the recent Schönrock values is shown to be within  $\pm$  one unit in the fifth place of refractive index.

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<sup>1</sup> *Z. Ver. deut. Zucker-Ind.*, 83, 892 (1933).

F. R. Bachler, before the American Chemical Society in September, 1933, described a method of analysis of sugar products specifying aliquots of a normal weight solution for the several determinations. In Bachler's method the refractometric measurements are made with the new Zeiss refractometer described above.

#### DRYING METHODS

The method for the determination of moisture in sirups and viscous materials of E. W. Rice and P. Boleracki,<sup>1</sup> which makes use of films of the material on thin sheets of silver, is shown to give constant weights after 2 to 4 hours of vacuum drying at 70°C.

It is recommended<sup>2</sup> that this method be further studied.

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#### REPORT ON POLARISCOPIC METHODS

By S. BYALL (Bureau of Chemistry and Soils, U. S. Department of Agriculture, Washington, D. C.), *Associate Referee*

Carrying out the suggestion approved at the last meeting of the Association, the Associate Referee continued the study of commercial invertase preparations to determine their suitability for analytical work.

The same five commercial preparations manufactured by the four companies which furnished the invertase preparations last year were again used and compared with an invertase solution prepared by the official method. All invertase preparations were diluted previous to use to an activity of approximately  $K=0.1$ , with water in the case of invertase preparation No. 1, official method, and with glycerine (approximately 65 per cent) in cases of Nos. 2 to 5, inclusive. Invertase No. 6, being dry or scale invertase, was diluted with water.

F. W. Zerban, who collaborated in this work, found difficulty in getting complete hydrolysis this year in some cases and suggested the use of 10 cc. of invertase solution of an activity of  $K=0.1$  instead of 5 cc., as recommended in the methods of the A.O.A.C. The Associate Referee recommends the use of 10 cc. in future work. There was also some difficulty experienced in getting clear solutions, and especially was this true in the case of the pure sucrose (Domino Cube).

Table 1 gives the results for the different products and for the different invertase preparations.

Although in some cases the differences in the individual results are great, the differences between the highest average and lowest average for the two years that this work has been carried out remain constant.

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<sup>1</sup> *Ind. Eng. Chem. Anal. Ed.*, 5, 11 (1933).

For report of Subcommittee A and action of the Association, see *This Journal*, 17, 45 (1934).

TABLE 1.—*Sucrose in sugar products determined by commercial invertase*  
(Results expressed in percentage)

COLLABORATORS	PRODUCT	INVERTASE PREPARATIONS					
		1	2	3	4	5	6
	Sucrose						
Byall	Domino C	99.92	100.0	100.07	99.92	100.00	100.02
Gamble		99.71	99.92	99.63	99.72	99.82	99.86
Mull		99.77	99.93	99.93	99.95	100.00	99.82
Av.		99.80	99.95	99.88	99.86	99.94	99.90
	Raw Sugar						
Byall		96.89	97.04	97.04	97.04	96.89	96.79
Gamble		96.35	96.54	96.51	96.54	96.36	96.23
Mull		96.36	96.56	96.56	96.57	96.51	96.18
Av.		96.43	96.71	96.70	96.72	96.58	96.40
	Molasses						
Byall		38.45	38.60	38.60	38.91	38.45	37.82
Gamble		38.01	38.23	38.09	38.15	38.07	38.01
Mull		38.00	38.19	38.12	38.13	38.15	38.04
Av.		38.15	38.34	38.27	38.39	38.22	38.96

It is recommended<sup>1</sup> that this work be continued for another year before any of the commercial preparations are recommended for approval by the Association.

TABLE 2.—*Differences between highest and lowest averages*

	DOMINO CUBE	RAW SUGAR	MOLASSES
	<i>per cent</i>	<i>per cent</i>	<i>per cent</i>
1932	0.16	0.33	0.36
1933	0.19	0.32	0.43

## REPORT ON CHEMICAL METHODS FOR REDUCING SUGARS

By R. F. JACKSON (U. S. Bureau of Standards, Washington, D. C.),  
*Associate Referee*

In a previous report the Lane-Eynon volumetric method<sup>2</sup> for reducing sugars was recommended for tentative adoption. This method specifies the use of methylene blue as an internal indicator, the dye being bleached sharply in the presence of a slight excess of reducing sugar. At the time of the recommendation the Lane-Eynon method had been but recently described and had not come into general use. It therefore seemed advisable

<sup>1</sup> For report of Subcommittee A and action of the Association, see *This Journal*, 17, 45 (1934).

<sup>2</sup> *Methods of Analysis*, A.O.A.C., 1930, 337; *J. Soc. Chem. Ind.*, 42, 32T (1923).



to retain the ferrocyanide method,<sup>1</sup> which it was designed ultimately to displace, during a transition period. At the present time the Lane-Eynon method has come into practically universal use and there appears to be no occasion for further retention of the ferrocyanide method. There is much objection to the latter method. As ferrocyanide must be used as an external indicator it is necessary to interrupt the reduction process in order to remove, filter, and acidify a portion of the reaction mixture for test. To arrive definitely at an end point this interruption must be repeated an indefinite number of times. In striking contrast to this procedure, the methylene blue method is carried out without interruption and a standard period of time of reaction can be closely approximated.

It is therefore recommended that paragraphs 32 and 33, page 377, of *Methods of Analysis*, A.O.A.C., 1930, which describes the ferrocyanide method, be discarded.

Among the methods now listed as "official" is the Soxhlet-Wein special method for lactose. This method was devised in the period of the early history of reducing sugar methods. After Fehling had shown that invert sugar could be determined quantitatively by its reducing effect upon alkaline copper solutions numerous investigators applied his principles to the determination of other reducing sugars. Unfortunately these other workers applied different analytical procedures, each of which was applicable to the sugar under investigation but inapplicable to other sugars. It was ultimately realized that a uniform procedure for all reducing sugars was not only desirable but even imperative because reducing sugars usually occur in mixtures whose analyses can only be accomplished by solving simultaneous equations in which different properties are represented.

The most comprehensive of these unified methods is that of Munson and Walker, which specifies the same analytical procedure for all sugars and supplies the respective copper-sugar equivalents. The essential difference between these two methods is in the duration of the period of boiling. Munson and Walker specify two minutes, while the Soxhlet-Wein method requires six minutes for the reaction. It is of interest to see what effect the difference in reaction time has upon the weight of precipitated copper. A series of reduction experiments with 175.2 mg. of lactose hydrate was conducted in which the time of boiling was 1.5, 2, 3, 4.5, and 6 minutes. The copper precipitated was 224.5, 226.3, 228.5, 232.4, and 234.5 mg., respectively. The weight of copper was related to the time of boiling by the method of least squares and the resulting equation,  $Cu = 219.3 + 3.79t - 0.2084t^2$ , was differentiated with respect to time. At the 2-minute point the precipitate was increasing at the rate of 2.9 mg. per minute, while at the 6-minute point it increased at the rate of 1.3 mg. per minute. An error in time would cause a slighter error in the Soxhlet-Wein method than in the Munson and Walker method. The difference, however, is not

<sup>1</sup> *Methods of Analysis*, A.O.A.C., 1930, 377.

great enough to justify retention of the special Soxhlet-Wein method, particularly as its use is practically limited to pure lactose and fresh milk, both of which can be analyzed satisfactorily by any of the general methods.

It is therefore recommended<sup>1</sup> that paragraphs 55 and 56, page 384, and Table 13, page 523, of *Methods of Analysis*, A.O.A.C., 1930, be discarded.

A paper on the Munson-Walker method was also prepared by the Associate Referee (see p. 293).

## REPORT ON FEEDING STUFFS

By V. E. MUNSEY (U. S. Food and Drug Administration, Washington, D. C.), *Referee*

Last year the Association voted to have studied in the regular way the subjects of Fat in Dairy Products Used As Feeds and Detection of Mineral Adulterants in Feeding Stuffs. An associate referee was appointed to study the former subject. Three general methods for determining fat in dairy products outlined by the Associate Referee were sent out for collaborative study. Results of this work did not definitely indicate any significant difference in the amount of fat determined by the different methods. The detection of mineral adulterants in feeding stuffs is so closely related to stock feed adulteration that it was thought no new referee should be appointed and that the Associate Referee on Stock Feed Adulteration should handle the whole subject.

The work on mineral mixed feeds, solvents for determination of fat in feeding stuffs, biological methods for detecting cod liver oil in feed mixtures, and hydrocyanic acid in glucoside-bearing material, was continued along the same lines as reported last year. It is given in detail by the associate referees.

After many years of collaborative work directed by the Associate Referee on Moisture, official methods were adopted for determining moisture in feeding stuffs by drying with heat in vacuum and by the electric oven method at 135°C. As a result of quite unsatisfactory results for moisture on some samples sent to more than 50 chemists for check analysis it seemed a little survey to find out the reason for such variation might be worth while. This work was undertaken this year by the Associate Referee on Moisture, and details of this work are given in his report. The majority of chemists seem to have their way of determining moisture and do not follow the official method. Such a condition is discouraging to those interested in uniformity. The moisture methods are somewhat empirical as are many other A.O.A.C. methods, and unless all determinations are carried out exactly the same, close agreements can not be expected. There

<sup>1</sup> For report of Subcommittee A and action of the Association, see *This Journal*, 17, 45 (1934).

is sufficient evidence to show that the same condition exists relative to the determination of fat, crude fiber, ash, etc.

So far as the Referee knows there has never been any collaborative work done on the method for determining sugars in the chapter under Grains and Stock Feeds. Therefore, it is recommended that an associate referee be appointed to study the methods for preparation of solution and determination of sugar in feeding stuffs.

The Referee concurs in the recommendations submitted by the associate referees, and in addition recommends<sup>1</sup>—

(1) That an associate referee be appointed to study methods applicable to the determination of fluorine in mineral feeds in collaboration with the Referee on Fluorine in other products.

(2) That an associate referee be appointed to study the mechanical method of separation outlined by the Bureau of Agricultural Economics for the classification of alfalfa products.

(3) That in the determination of moisture the method of drying in a current of  $H_2$  at atmospheric pressure be dropped, as this method is not in general use.

## REPORT ON STOCK FEED ADULTERATION

By H. E. GENSLE (Department of Agriculture, Harrisburg, Pa.),  
*Associate Referee*

The Associate Referee communicated with analysts interested in the microanalytical examination of feeding stuffs and requested them to collaborate in the trial of a method for detecting potassium iodide in mixed feeds. This modification was devised because the method previously submitted to collaborators, although yielding excellent results, was questioned as to its value when potassium iodide was added in a spraying process, instead of simple admixture. The revised method follows:

### DETECTION OF IODINE IN FEEDING STUFFS

Run the original unground sample through a 30-mesh sieve. Place the amount of this sifted material ordinarily used on a microscopic slide and mount in 5% sulfuric acid. Add a small fragment of sodium nitrite and a very small quantity of starch (in case of feeds containing none) and immediately place the cover-glass thereon. Warm cautiously and examine the slide for the presence of starch grains which have been affected by the starch-iodine reaction, indicated by a bluish coloration. (This color may be very faint and require examination with a higher powered objective for verification, and it may be necessary to examine several slides before final conclusions as to the presence or absence of iodine can be made.)

The collaborators were requested to examine samples of commercial feeding stuffs in which the manufacturers claimed the presence of iodine

<sup>1</sup> For report of Subcommittee A and action of the Association, see *This Journal*, 17, 46 (1934).

and report whether or not a positive reaction was obtained. They were also instructed to apply the method to feeding materials that were known to be free from iodine, such as soybean meal, wheat bran, etc., and also to manufactured brands and feeds in which iodine is an ingredient and report the results.

As a result of the work done with this method according to the instructions outlined, it is quite evident that the method did not meet with success, because all the analysts reported either that they did not get a positive reaction or that the reaction was so indefinite as to be doubtful.

Several of the collaborators reported that they were using with satisfactory results the method for the detection of iodine submitted in 1931.

No work was done on mineral adulterants in feeding stuffs as recommended at the last meeting.

#### RECOMMENDATIONS<sup>1</sup>

It is recommended—

(1) That further study be given to the microanalytical detection of iodine in feeding stuffs.

(2) That a study of the detection of mineral adulterants in feeding stuffs be made.

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### REPORT ON MINERAL MIXED FEEDS

By H. A. HALVORSON (Department of Agriculture Dairy and Food, St. Paul, Minnesota), *Associate Referee*

Samples and directions for the 1933 work on mineral mixed feeds were sent to 22 chemists who had signified a willingness to take part. They were instructed (1) to determine iodine on three samples by the method of Knapheide and Lamb,<sup>2</sup> and by other proposed methods, particularly the micro-modification of the McClendon combustion method;<sup>3</sup> and (2) to determine calcium oxide in Samples 2 and 3 by the present tentative method<sup>4</sup> and by the procedure proposed by Meloche, Clifcorn and Griem.<sup>5</sup>

#### DESCRIPTION OF SAMPLES

Sample 1 was ground dried kelp. It was part of the same lot from which Sample 1 in the 1932 collaborative work was obtained. The mean of 20 iodine averages reported on this sample in 1932 was 0.138 per cent, and 90 per cent of the collaborators that year obtained averages within  $\pm 0.010$  per cent of this mean.

Sample 2 was in part a mixture of chemically pure ingredients and con-

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<sup>1</sup> For report of Subcommittee A and action of the Association, see *This Journal*, 17, 47 (1934)

<sup>2</sup> *J. Am. Chem. Soc.*, 50, 2121 (1928).

<sup>3</sup> *Ibid.*, 52, 980 (1930).

<sup>4</sup> *Methods of Analysis*, A.O.A.C., 1930, 287.

<sup>5</sup> *This Journal*, 16, 240 (1933).

sisted of 40 per cent tribasic calcium phosphate (precipitated), 40 per cent calcium carbonate (precipitated chalk), 19.95 per cent salt (sodium chloride C.P.), and 0.05 per cent potassium iodide. Calculation of the iodine content, from the amount of potassium iodide added, showed it to be 0.0382 per cent. Calcium oxide in Sample 2, calculated from determinations made on each of the ingredients by A. O. Olson of the Associate Referee's laboratory, was found to be 42.59 per cent by the tentative A.O.A.C. method, and 42.68 per cent by the method of Meloche, Clifcorn and Griem. Collaborators Griem and Clifcorn reported 42.16 per cent calcium oxide in this sample by the gravimetric method. It is believed that the less satisfactory agreement in both the iodine and calcium oxide results reported on Sample 2 compared with Sample 3 was due to the difficulty of obtaining a uniform mixture in the presence of the clay-like pastiness of the calcium carbonate (precipitated chalk) used.

Sample 3 had the following composition: 10 per cent digester tankage, 10 per cent charcoal, 25 per cent spent bone black, 35 per cent ground limestone, 19.9 per cent salt (sodium chloride C.P.), and 0.1 per cent potassium iodide. This sample was made to simulate commercial mineral feeds found on the market, and although the mixture in appearance seemed to lack uniformity, the ingredients were granular and of such nature as to cause little difficulty in obtaining an even distribution of the components. Calculation of the iodine content, from the potassium iodide added, resulted in a figure of 0.0764 per cent. Calculations of the calcium oxide content of Sample 3, in the same manner used with Sample 2, showed it to contain 31.82 per cent by the tentative method, 31.73 per cent by the proposed method, and 31.42 per cent by the gravimetric method.

The calculated calcium oxide contents for Samples 2 and 3, inserted in the heading of Table 2, are the means of the results obtained on analysis of the ingredients by the tentative method and the proposed method.

#### DISCUSSION OF IODINE RESULTS

In Table 1 only the averages are shown, although most of the chemists reported results from two to ten determinations on each sample. A lack of satisfactory agreement between some of the averages reported is believed to be due to personal errors or to the sample, rather than to a faulty method.

The mean of the 20 averages reported on Sample 1 is 0.144 per cent after figures beyond the third decimal place are dropped; 65 per cent of the averages are within  $\pm 0.005$  per cent of this mean, which compares with 55 per cent obtained by a similar calculation on the same product last year. The slightly higher mean obtained from the averages this year can probably be explained by the loss of moisture from the kelp during storage.

TABLE 1.—*Iodine in mineral feed samples by Knapheide-Lamb method*  
(Results expressed in percentage)

COLLABORATORS	SAMPLE 1	SAMPLE 2 0.0382% ADDED	SAMPLE 3 0.0764% ADDED
	<i>Average</i>	<i>Average</i>	<i>Average</i>
A. W. Clark Geneva, N. Y.	0.142	0.0322	0.0739
W. P. Elmslie and Paul Caldwell Moorman Mfg. Co. Quincy, Ill.	0.141	0.0359	0.0793
G. S. Fraps and T. L. Ogier College Station, Texas	0.1324	0.0309	0.0711
Guy G. Frary and H. E. Lacy Vermillion, S. D.	0.140	0.035	0.073
W. C. Geagley Lansing, Mich.	0.138	0.038	0.0833
W. B. Griem and LaVerne Clifcorn Madison, Wis. (1 gram)	0.1484		
(2 gram)	0.1396	0.0360	0.0784
W. F. Hand and H. Solomon A & M College, Miss.	0.147	0.041	0.068
A. P. Kerr and W. P. Denson Baton Rouge, La.	0.108	0.035	0.074
H. R. Kraybill and Halliday Lafayette, Ind.	0.143	0.028	0.078
C. S. Ladd and W. A. Groves Bismarck, N. D.	0.1858	0.0485	0.0908
H. W. Loy, Jr. and H. H. King Manhattan, Kan.	0.1425	0.0293	0.1030
R. C. Newton Swift & Co. Chicago, Ill.	0.148	0.033	0.078
A. O. Olson St. Paul, Minn.	0.139	0.034	0.075
E. L. Redfern Des Moines, Ia.	0.1469	0.0268	0.0828
W. R. Roy Lexington, Ky.	0.167	0.040	0.080
H. D. Spears Lexington, Ky.	0.1431	0.0390	
H. P. Strack Nashville, Tenn.	0.1229	0.0225	0.0608
J. J. Vollertsen Armour & Co. Chicago, Ill.	0.140	0.029	0.080
D. W. Young Lexington, Ky.	0.158	0.031	0.080

The mean of the iodine averages reported on Sample 2 is 0.004 per cent less than the percentage of added iodine; 68 per cent of the reported aver-

ages are within  $\pm 0.005$  per cent of this mean, which was found to be 0.034 per cent. Considering the small percentage of iodine added this showing does not appear so good as that on Samples 1 and 3.

The mean of the eighteen iodine averages on Sample 3 is 0.078 per cent, which is only 0.002 per cent greater than the quantity of iodine added; 67 per cent of the reported averages are within  $\pm 0.005$  per cent of the mean.

The Associate Referee and several of the collaborators believe that sufficient work has been done with the Knapheide and Lamb method to warrant the recommendation that it be adopted as a tentative method. There is, of course, the possibility that with sufficient study other methods might prove equally satisfactory and more accurate. It is pertinent, however, to call attention to the fact that for several years the Associate Referee has invited collaborators to make determinations for iodine on the A.O.A.C. samples by methods other than the Knapheide and Lamb procedure. With very few exceptions they have limited their work to the Knapheide and Lamb method, and this is assumed to be evidence of its practical nature for use on mineral mixtures.

#### DISCUSSION OF CALCIUM OXIDE RESULTS

In Table 2 only the averages are recorded, although many of the analysts made from one to six determinations on the two samples by each method. From the results obtained, there seems to be little to choose between the two methods. Several of the collaborators expressed a preference for the present tentative method over the proposed method because of its greater simplicity and convenience. No doubt further work might be undertaken with the view to adopting either one or the other as the official method.

Only two of the eighteen collaborators stated whether the results reported were made on aliquots of the same weighing or on different weighings. Omitting from consideration the results reported by two collaborators, it is found that the differences between the high and low individual results are in most cases within experimental error. The greatest difference reported by any one analyst is 0.57 per cent on Sample 2 and 0.29 per cent on Sample 3. Most of the others are much less.

Using the tentative A.O.A.C. method, A. O. Olson also conducted a series of tests to determine the differences between the maximum and minimum calcium oxide results obtained on aliquots from both the same weighing and from different weighings. The maximum spread between determinations made from four separate weighings of Sample 2 was 1.00 per cent. Determinations made on the aliquots from the same weighings in this series of four showed the maximum spread to be only 0.18 per cent. A similar test on Sample 3 showed the maximum spread between results from four different weighings to be 0.51 per cent; on aliquots from the

same weighings the greatest difference was 0.26 per cent. It is believed that this test proves that the discrepancies in the results obtained with the tentative method are due to errors in sampling and mixing rather than to faults of the method.

TABLE 2.—*Calcium oxide in mineral feed samples*  
(Results expressed in percentage)

COLLABORATORS	SAMPLE 2—CaO CALCULATED FROM ANALYSIS OF INGREDIENTS—42.64%		SAMPLE 3—CaO CALCULATED FROM ANALYSIS OF INGREDIENTS—31.78%	
	A.O.A.C. METHOD	PROPOSED METHOD	A.O.A.C. METHOD	PROPOSED METHOD
	<i>Average</i>	<i>Average</i>	<i>Average</i>	<i>Average</i>
L. E. Bopst and R. E. Baumgardner College Park, Md.	42.28	42.56	31.27	31.20
A. W. Clark	41.66	40.45	30.47	30.09
G. S. Fraps and H. W. Walker	42.71		31.89	
W. C. Geagley	43.33	43.18	31.77	31.64
W. B. Griem and LaVerne Clifcorn	41.75	42.18	31.07	31.38
W. F. Hand and H. Solomon	42.04	42.18	31.32	31.25
H. R. Kraybill and Halliday	42.58	42.12	31.37	31.37
C. S. Ladd and W. A. Groves	42.06	41.54	32.10	31.54
H. W. Loy, Jr. and H. H. King	43.09		31.37	
V. E. Munsey Washington, D. C.	41.68	41.75	31.54	31.37
R. C. Newton	41.62	41.58	31.06	30.81
A. O. Olson	41.88	41.91	31.46	31.28
H. D. Spears	42.63	42.52	32.71	32.96
E. L. Redfern	42.68	42.19	31.91	31.62
W. R. Roy	42.35		31.66	
O. M. Shedd	41.79		31.04	
J. J. Vollertsen			31.12	31.44
D. W. Young	42.00		31.08	

Results were received from J. W. Bowen and J. Drain of Purina Mills, St. Louis, Missouri, too late to be included in the table. They report the following average percentages for iodine: No. 1, 0.130; No. 2, 0.034; No. 3, 0.077. Their calcium oxide average percentages by the two methods are: No. 2, tentative, 41.92—proposed, 41.97; No. 3, tentative, 30.91—proposed, 31.03.

#### RECOMMENDATIONS<sup>1</sup>

It is recommended—

(1) That the Knapheide and Lamb method for the determination of iodine in mineral mixed feeds be adopted as tentative.

(2) That the study of this method and of other methods for this determination be continued.

<sup>1</sup> For report of Subcommittee A and action of the Association, see *This Journal*, 17, 47 (1934).



(3) That studies of methods for the determination of calcium oxide in mineral mixed feeds be continued.

## REPORT ON MOISTURE IN FEEDING STUFFS

By G. E. GRATTAN (Department of Agriculture, Ottawa, Canada),  
*Associate Referee*

The Associate Referee was instructed to make a survey of the methods used for the determination of moisture in the various feed control laboratories in this Association. A questionnaire was sent to all known labora-

TABLE 1.—*Ovens*

KIND OF OVEN	NUMBER IN USE	
	VACUUM	NON-VACUUM
Electrically heated	22	19
Gas-heated	3	—
Water-jacketed	2	1 with dry H.
Steam-heated	—	2

TABLE 2.—*Drying periods*

DRYING	NO. OF LABORATORIES	DRYING	NO. OF LABORATORIES
<i>hours</i>		<i>hours</i>	
2	6	6-8	1
3½-5	1	10	1
4-5	2	15-16	2
4-6	1	16-20	1
5-6	30	Overnight	2
		To constant wt.	1

tories, and replies were received from 47. The information gathered is quite enlightening and shows reasons why results vary from 4.5 to 8.25 per cent on a sample containing approximately 6.75 per cent moisture. So great were the variations in methods that it was not possible to condense them in one table. Practically every laboratory uses a different method. In fact, some laboratories use two different ovens and two different sets of dishes. Replies were tabulated as follows to show (1) kind of oven and number in use; (2) drying periods; (3) temperatures; and (4) size (approximate) and kind of containers.

Covered flat-bottomed dishes, about 3 inches in diameter, appear to be favored. When small crucibles, thimbles and glass tubes are used, a low moisture content is probably found. Forty-five laboratories use 2 grams for analysis, one uses 1 gram, and one uses 5 grams.

The amount of vacuum used in laboratories where the vacuum oven method is used appears to be whatever the pump will pull. The answers were given in so many different ways that it was difficult to correlate them. They varied from 20 pounds to 21-30 inches, 100 to 533 mm., and to 3-4 mm. Some stated "as much as we can get."

TABLE 3.—*Temperatures*

TEMPERATURE	VACUUM OVENS	AIR OVENS
°C.		
65	1	—
85	1	—
90	1	—
95	—	1
96	1	1
98-99	8	3
100	11	9
101-105	2	4
110	—	1
135	—	3
No thermometer (boiling water)	1	

TABLE 4.—*Containers*

KIND	SIZE	NUMBER
	<i>diameter in inches</i>	
Dishes, aluminum, covered	2 -3½	31
Dishes, aluminum, not covered	2	3
Crucibles, porcelain, not covered	1½-1½	5
Crucibles, alundum, not covered	1½	1
Watch-glasses, not covered	3	3
Dishes, glass, covered	3	1
Dishes, platinum, not covered	2½-3½	2
Extraction shells, paper, not covered	1	1
Extraction tubes, glass, not covered	¾	1

RECOMMENDATIONS<sup>1</sup>

It is recommended—

- (1) That the temperature of the vacuum oven in moisture determinations be 95°-100°C. outside the vacuum chamber.
- (2) That covered aluminum dishes not less than 50 mm. in diameter and not over 40 mm. deep be used.
- (3) That the method of drying in a current of hydrogen at atmospheric pressure be dropped, as this method is not used.

<sup>1</sup> For report of Subcommittee A and action of the Association, see *This Journal*, 17, 47 (1933).

REPORT ON BIOLOGICAL METHODS FOR DETERMINATION  
OF COD LIVER OIL IN FEED MIXTURES

By W. B. GRIEM (Department of Agriculture and Markets, Madison,  
Wisconsin), *Associate Referee*

Two previous reports<sup>1</sup> under this subject have been presented to the Association. The work was limited to the establishment of a method for biologically assaying vitamin D carriers (feeding) for vitamin D potency.

TABLE 1.—*Collaborative results*

COLLABORATORS	CALCIUM- PHOSPHORUS (Ca/P) RATIO			AVERAGE GROUP ASH OF MOISTURE- AND FAT-FREE TIBIAE FOR BASAL RATIONS AND FOR BASAL RATIONS FORTIFIED WITH COM- POSITE SAMPLE OF COD LIVER OIL					
	Ca	P	Ca/P	BASAL	BASAL PLUS—				
					1/16 OF 1%	1/8 OF 1%	1/4 OF 1%	1/2 OF 1%	1%
	per cent	per cent	per cent	per cent	per cent	per cent	per cent	per cent	per cent
F. E. Booth Company Biological Laboratory Berkeley, Calif.	0.87	0.61	1.33	38.0	—	42.5	46.1	46.1	—
State Inspection Service University of Maryland College Park, Md.	—	—	—	35.2	40.7	44.3	46.0	45.7	46.6
Feed and Fertilizer Control Minnesota Dept. Agr. St. Paul, Minn.	0.85	0.69	1.23	30.8	34.2	37.9	46.6	47.8	47.5
Feed and Fertilizer Div. Wisconsin Dept. Agr. & Markets Madison, Wis.	0.85	0.65	1.31	34.2	39.2	43.5	45.5	46.4	46.3
Feed and Fertilizer Div. Wisconsin Dept. Agr. & Markets Madison, Wis.	0.87	0.68	1.28	32.5	33.6	42.1	46.2	—	47.0

The Associate Referee was instructed to study any methods which might have been suggested for the detection of cod liver oil in mixed feeds. No method was suggested, and he was unable to devote any time to an original study.

The other recommendation instructed him to modify the method for vitamin D assay as incorporated in last year's report, and to have the method studied collaboratively. Details of the method were changed in accordance with suggestions made, the most important one being the shortening of the feeding period from 5 weeks to 4 weeks, based on the

<sup>1</sup> *This Journal*, 15, 222 (1932); 16, 184 (1933).

findings of Lachat, Halvorson, and Palmer.<sup>1</sup> The Hart<sup>2</sup> basal rachitic ration was also slightly modified so as to include iodized salt instead of ordinary salt. The method has been published.<sup>3</sup>

After the method had been revised collaborative work was inaugurated. Equal parts of 13 different brands of cod liver oil samples (feeding), which had been collected from retail stocks in Wisconsin, were mixed.

The composite sample was found to contain 40 Steenbock Vitamin D units per gram by biological rat assay. Portions of this composite sample were submitted to three collaborators for assay. A portion was also assayed in the laboratory of the Associate Referee at the time the samples were sent out, and the assay was repeated several months later with birds from a different source. For this second assay new ingredients were purchased for compounding the basal ration.

Collaborators were asked to assay the sample at five different levels so that the minimum level at which complete antirachitic protection was obtained could be determined. Several collaborators also reported the calcium and phosphorus content of the basal rations, which are shown in Table 1, as are also the Ca/P ratios.

#### DISCUSSION

From the calcium and phosphorus content of the various basal rations it appears that there is excellent uniformity in the Ca/P ratios, which range from 1.23 to 1.33, as well as in the total amounts of the elements. This close agreement would indicate that the basal ration can very easily be duplicated without a material variation in the important Ca/P ratio. Agreement in the calcium and phosphorus content of basal rations is considered to be essential in assay work of this kind.

In the opinion of the Associate Referee, the collaborative results are in very good agreement. In every assay complete antirachitic protection was produced when 1/4 of 1 per cent of the composite oil was added to the basal rations, and incomplete protection was produced at the 1/8 of 1 per cent level. Further additions of the oil did not materially improve calcification. The table indicates that the maximum variations in the percentage of ash at the different levels was as follows: 7.2 in basal groups; 7.1 at 1/16 of 1 per cent level; 6.4 at 1/8 of 1 per cent level; 1.1 at 1/4 of 1 per cent level; 2.1 at 1/2 of 1 per cent level; and 1.2 at 1 per cent level. It is apparent that in spite of great variations in the bone ash in the basal groups and at 1/16 and 1/8 of 1 per cent levels uniformity of final results can be obtained.

The wide variations in the basal groups indicate that when interpreting calcification data, deviations from positive controls should be considered of equal if not of more importance than deviations from the basal groups.

<sup>1</sup> *Science*, 73, 710 (1931).

<sup>2</sup> *Ibid.*, 15, 660 (1932).

<sup>3</sup> *This Journal*, 17, 69 (1934).

## APPLICATION OF METHOD

Table 2 shows some typical results that were obtained this past year in the laboratory of the Associate Referee. The samples were collected from retail stocks in Wisconsin, by agents of the Department of Agriculture and Markets. The results show the great variation in the potencies of the different cod liver oils. Sample 3 is easily four times more potent in vitamin D than Sample 1. It is probably twice as potent as Sample 2. Also Sample 2 is twice as potent as Sample 1.

TABLE 2.—Results obtained in laboratory of Associate Referee

RATION	AVERAGE GROUP ASH OF MOISTURE- AND FAT-FREE TIBIAN			
	BASAL	COD LIVER OIL NO. 1	COD LIVER OIL NO. 2	COD LIVER OIL NO. 3
	<i>per cent</i>	<i>per cent</i>	<i>per cent</i>	<i>per cent</i>
Basal Ration	34.2	—	—	—
Basal plus $\frac{1}{2}$ per cent Oil		48.4	39.1	45.5
Basal plus $\frac{1}{4}$ per cent Oil		39.1	45.0	45.8
Basal plus $\frac{1}{8}$ per cent Oil		44.5	45.4	46.8

## SUMMARY

This method of assay has been extremely useful in determining comparative vitamin D potencies of many vitamin D carriers. It has been instrumental in detecting gross misrepresentation of others, some of them actually worthless as vitamin D supplements. The method is being used in control work in several feed control laboratories. Very good agreement in results was obtained in collaborative work. It would facilitate control work to have this method established and recognized by this Association.

RECOMMENDATIONS<sup>1</sup>

It is recommended—

- (1) That the method of vitamin D assay discussed in this report to be adopted as tentative.
- (2) That the method be subjected to further study, collaboratively, if feasible.
- (3) That biological detection of vitamin D carriers in mixed feeds be studied.

## REPORT ON HYDROCYANIC ACID IN GLUCOSIDE-BEARING MATERIALS

By GORDON SMITH (U. S. Food and Drug Administration, Washington, D. C.), *Associate Referee*

To test the accuracy of the present tentative methods for the determination of hydrocyanic acid<sup>2</sup> a sample of linseed meal was sent to twelve

<sup>1</sup> For report of Subcommittee A and action of the Association, see *This Journal*, 17, 46 (1934).

<sup>2</sup> *Methods of Analysis*, A.O.A.C., 1930, 287.

collaborators. Six were asked to use the alkaline titration method and the Prussian blue method. Reports were received from three of these and from another collaborator who ran the Prussian blue method only. Six were

*Collaborative results*

COLLABORATOR	ALKALINE TITRATION METHOD	PRUSSIAN BLUE
	p.p.m.	p.p.m.
(1)	120	113
(2)	263.2	259
	260.6	247
		247
		247
(3)	335	105
	344	140
		105
(4)		80
		83
(5)	170	107
(Referee)	176	111

	MODIFIED ALKALINE TITRATION METHOD	ACID TITRATION METHOD	GRAVIMETRIC METHOD
(1)		108.0 110.5	90.5 92.8
(2)	998	97	
	1033	111	
	1012	108	
	1014	105	
(3)	172	118	
	194	118	
	183	100	
	189		
(4)	288	143	
	274	141	
(5)	168	135	
(Referee)	141	142	

asked to use the acid titration method and a slight modification of the alkaline titration method. Reports were received from four collaborators.

The results obtained by the acid titration method vary, at the extremes, from 97 to 143 p.p.m.; those by the Prussian blue method vary from 80

to 259. A majority of the results, however, fall within a much narrower range. Results by the alkaline titration method vary from 120 to 1033 p.p.m. and are irregularly distributed. The end point in this method is so obscure and indefinite that it is a matter of guess work. The slight modifications in the method submitted to half of the collaborators gave no better results.

Some of the comments of collaborators follow:

The end point by the alkaline titration method is poor.

We feel that the statement "the first permanent turbidity" in the alkaline titration method is insufficient and misleading. In other words, had we not tried the method on a standard HCN sample, we would have considered the end point when the sample became milky. However, to check our standard, it was necessary to consider the end point as the reading which showed the slightest color change in the solution. Consequently the end point was determined on the sample in this manner. This point was very difficult to determine.

We feel that a more detailed explanation should be given in the Prussian blue method relative to making up the standard HCN solution, and that a caution should be inserted in the method regarding the speed with which the Prussian blue settles.

Rather poor end point in alkaline titration method.

We believe that the alkaline titration method, which is, in the main, Liebig's method, was not intended to be accurate at such low concentrations as are found here, especially in the presence of volatile organic compounds, which cause a darkening of the solution, due to the reduction of silver ion.

This last comment, by Clifcorn, states precisely the shortcomings of the alkaline titration method. It is not suitable for the determination of such small quantities of hydrocyanic acid, and the Associate Referee does not believe that it should be retained as an official method.

Clifcorn also recommends the following gravimetric method, with which he obtained good results on the linseed meal sample:

Introduce 10-20 grams of the ground material into an 800 cc. Kjeldahl flask, add 200 cc. of water and slowly pass air through the mixture for 2 hours. Place the flask in boiling water and distil with steam, collecting the distillate in 20 cc. or more of an approximately 0.02 *N* Ag NO<sub>3</sub> solution to which 1 cc. of concentrated HNO<sub>3</sub> has been added. Distil over about 150 cc. Filter the precipitate through a previously ignited and tared Gooch crucible and wash the precipitate with water. Ignite at red heat to metallic silver and weigh as such. Calculate results as p.p.m. 1 mg. of Ag = 0.2503 mg. of HCN.

This method has the advantage of eliminating difficult end points, and may prove to be more accurate than the present methods.

#### RECOMMENDATIONS<sup>1</sup>

It is recommended—

- (1) That the alkaline titration method be dropped.
- (2) That the Prussian blue and acid titration methods, and also Clifcorn's gravimetric method, be given further study.

<sup>1</sup> For report of Subcommittee A and action of the Association, see *This Journal*, 17, 47 (1934).

(3) That in the last sentence under the Prussian blue method (*Methods of Analysis*, A.O.A.C., 1930, 287), the words "from a standard soln containing 1 mg of KCN diluted to 25 cc.," be changed to read, "from the vacuum evaporation of a standard soln containing 1 mg of KCN diluted to 25 cc.," and that the following words be added: "This solution = 0.415 mg. of HCN." These changes are made for the sake of greater clearness.

## REPORT ON FAT IN FEEDING STUFFS

By L. S. WALKER (Agricultural Experiment Station, Burlington, Vermont), *Associate Referee*

Last year 30 different types of feeding stuffs were compared, anhydrous ether and dichloromethane being used as fat solvents, and on the average 0.23 per cent more fat was recovered with dichloromethane. As this work indicated that the new solvent should receive favorable consideration, further study was recommended.

Directions were sent to 17 chemists for collaborative work. It was suggested that several typical feeds and the four American Association of Feed Control Officials check samples be used, that fat determination be made by the official method (*Methods of Analysis*, A.O.A.C., 1930, p. 279), and that both anhydrous ether and dichloromethane be used as solvents.

Reports were received from the following collaborators. Their results appear under their respective numbers in the tables which follow.

1. W. T. Mathis, Agr. Exp. Station, New Haven, Conn.
2. L. V. Taylor, Jr., Dept. of Agr., Jefferson City, Mo.
3. J. J. Vollertsen, Armour & Co., Chicago, Ill.
4. A. B. Heagy, Regulatory Service, College Park, Md.
5. G. E. Halliday, Agr. Exp. Station, Lafayette, Ind.
6. V. E. Munsey, U. S. Dept. Agr., Washington, D. C.
7. E. F. Boyce, Regulatory Service, Burlington, Vt.

## COMMENTS OF COLLABORATORS

*L. V. Taylor, Jr.*—Considerable difficulty was experienced in obtaining duplicate checks when dichloromethane was used . . . It is noted from our results that there is a wide variation in the percentage of extract found in meat products. We offer no explanation for this variation, but might add that the physical appearance of the two extracts was indistinguishable.

*J. J. Vollertsen.*—The dichloromethane gives higher results than our ordinary solvent does, and in some cases more than ethyl ether. Because of this and its high cost we do not recommend its adoption as a fat solvent.

*A. B. Heagy.*—Dichloromethane requires 50–55 minutes to dry after extraction and ethyl ether 40 minutes. With two exceptions, the 21 samples used ran higher with dichloromethane than with ether. Special note should be taken of the meat scraps sample, which ran 1.30 per cent higher with dichloromethane. Fiber was



TABLE 1.—*Dichloromethane and anhydrous ether as fat solvents in feeding stuffs*

COLLABORATORS		1	2	3	4	5	6	7	AV.
Bran	D	5.56	4.07		4.82	4.57	3.98	4.24	4.54
	E	5.55	4.61		4.58	3.93	3.78	4.00	4.41
Meat scraps	D		9.89	10.56	12.33	5.99	7.03	10.15	9.90
	E		8.57	10.35	11.03	5.47	5.99	10.19	9.28
Linseed meal	D	4.82	5.69		5.57		8.33	5.81	6.00
	E	4.55	5.39		4.98		8.07	4.99	5.50
C. S. meal	D	6.08	7.37		7.50			6.57	6.87
	E	5.80	7.16		7.24			6.35	6.64
Middlings	D	6.05	4.46		5.07			5.16	5.19
	E	5.85	4.76		4.73			4.98	5.08
Hominy	D	6.55			7.83	6.77		7.21	7.11
	E	6.43			7.60	6.60		7.20	7.00
Alfalfa	D		2.02		2.80	2.96		2.57	2.49
	E		2.03		2.16	1.85		2.12	2.05
Dairy feed	D	5.14	4.41		4.83			4.90	4.83
	E	4.92	4.54		4.43			4.80	4.74
Stock feed	D	1.70	3.95				4.01	4.12	3.64
	E	1.95	3.61				3.91	4.09	3.54
Soybean meal	D				4.56	18.15		6.38	8.87
	E				4.24	17.51		6.10	8.49
Gluten feed	D				3.39	2.81		3.80	3.52
	E				2.90	2.28		3.51	3.14
Mixed feed	D		4.79				3.90	4.35	4.35
	E		4.85				3.74	4.35	4.31
Beet pulp	D	.65			.47			.53	.55
	E	.58			.45			.52	.52
Brewers' grain	D	7.04			7.99			8.21	7.75
	E	6.53			7.16			7.62	7.10
Calf and Hog	D		4.93		4.61			4.87	4.84
	E		4.35		4.56			4.77	4.61
Scratch feed	D	2.78			3.67			2.64	2.93
	E	2.73			3.83			2.43	2.85

TABLE 1 (Continued)

COLLABORATORS		1	2	3	4	5	6	7	AV.
Mash	D	5.29			5.46			5.04	5.26
	E	5.36			5.31			4.91	5.12
Red dog flour	D				5.08			4.58	4.83
	E				5.00			4.48	4.74
Corn feed meal	D		4.86		7.61				5.77
	E		4.89		7.47				5.72
Corn meal	D		4.31					4.14	4.23
	E		4.04					4.07	4.06
Peanut meal	D		11.34		2.98				7.16
	E		10.19		3.02				6.97
Oat mill feed	D				2.38			1.76	1.96
	E				2.07			1.80	1.89
Gluten meal	D							3.81	3.81
	E							2.17	2.17
Rye feed	D							3.62	3.62
	E							3.40	3.40
Corn oil meal	D		6.51						6.51
	E		6.06						6.06
Corn bran	D		8.53						8.53
	E		8.51						8.51
Malt sprouts	D		2.61						2.61
	E		1.91						1.91
Grand Av.	D								5.10
	E								4.81

D—Dichloromethane

E—Ether

run after extraction with the two solvents under the same conditions and found to check within 0.20 per cent. All dichloromethane results were checked within 0.10 per cent, making it necessary to run some of the samples five times. The amount of dichloromethane recovered is about equal to that of ether, but it took twice the time for dichloromethane.

## DISCUSSION

The first table represents about 400 tests on 27 types of feeding stuffs. Each collaborator's results were averaged, and the figure in the last col-

umn is the average of all tests in its particular group. The averages of the 27 feedings stuffs ran higher by use of dichloromethane in every case. They vary from 1.64 per cent in gluten meal to 0.02 per cent in corn bran, with an average difference of 0.29 per cent; 66 per cent did not exceed 0.3 per cent difference on the two solvents. If, then, 0.30 per cent is taken as a reasonable difference for the two solvents, on individual cases 100 per cent of the reports on cottonseed meal, hominy, scratch feed, mash, beet

TABLE 2.—*Comparison of ether and dichloromethane as a fat solvent on A.A.F.C.O. check samples*

COLLABORATORS		1	2	3	4
		per cent	per cent	per cent	per cent
W. T. Mathis Connecticut	D			6.10	
	A			5.95	
A. B. Heagy Maryland	D	5.22			
	A	5.21			
E. P. Greene Florida	D	5.40	5.47	6.50	4.17
	A	5.32	5.40	6.15	4.05
G. E. Halliday Indiana	D	5.38	5.00	6.47	4.17
	A	5.25	4.77	5.85	4.00
H. E. Schlichting Michigan	D	5.24	5.05	6.30	4.14
	A	5.14	4.74	5.83	3.89
E. F. Boyce Vermont	D	5.70	5.37	6.54	4.74
	A	5.50	5.15	6.20	4.26
Average	D	5.39	5.22	6.38	4.31
	A	5.28	5.02	6.00	4.05

D—Dichloromethane

A—Anhydrous ether

pulp, wheat mixed feed, oat mill feed, corn feed meal, corn meal, wheat red dog flour, rye feed and corn bran; 75 per cent of the dairy and stock feeds; 66 per cent of the wheat bran, calf and hog, and soy bean meal; 60 per cent of linseed meals; and 50 per cent of the wheat middlings and peanut meals did not exceed 0.3 per cent difference for the two solvents; whereas, corn oil meal, alfalfa meal, brewers' dried grains, malt sprouts, meat scraps, gluten meal and feed were not so good. One might infer that on this last group anhydrous ether did not remove all the fat, for it has been noted that on several of these materials the physical appearance of the two extracts was apparently the same.

Table 3 shows a comparison of the two solvents on the American Association of Feed Control Official check samples. No. 3 was a cottonseed

meal and the others were proprietary feeds. The results show closer agreements on the whole than do those in the first two tables, ranging from 0.01 to 0.62 per cent differences.

It is evident that dichloromethane is as good a fat solvent as is anhydrous ether and the resulting extract as pure. However, every analyst seemed to have trouble in obtaining good checks with the new solvent. The cause for this has not been learned. Its non-explosive feature is in its favor as many injuries and fires have been attributed to ether fumes. This new solvent deserves careful consideration, and the Associate Referee believes that it has considerable merit. Before a tentative method specifying dichloromethane can be written into *Methods of Analysis*, however, the new solvent should be thoroughly standardized and more collaborative work done. This might clear up some of these difficulties.

#### GOLDFISCH EXTRACTION APPARATUS

This apparatus was developed recently to reduce the time of extraction. By its use a fat determination can be made in about 3 hours. H. H. Dewey (Dept. of Agr., Salem, Oregon) has done considerable work with this apparatus on all types of feeding stuffs. He says:

My work with the Goldfish Extractor and the Goldfish short time method for fat extraction in comparison with the official method has led to the following conclusions: (1) There is at least an equal accuracy and dependability; (2) there is a 3-hour period of extraction instead of a 16-hour period; (3) there is a material saving of solvent; (4) There is a material saving of time in recovery of the solvent.

L. V. Taylor, Jr. (Dept. of Agr., Jefferson City, Mo.) says:

We are finding this extraction very satisfactory and hope to see the official method changed in the near future.

Taylor also tested the four A.A.F.C.O. check samples with the Goldfish Extractor, using ether and dichloromethane as solvents. He says:

We experienced some difficulty in obtaining checks upon the use of dichloromethane on the Sargent Type B Extractor; however, this was eliminated on the Goldfish Extractor, all duplicates checking within 0.1 per cent. Although the results of the samples shown in the table failed to cover the wide range of agricultural products, it may be pointed out that the evidence from these results, and of many other products analyzed by this laboratory on the Goldfish Extractor, warrants careful consideration by the Association, with the view to altering the time limit in the official method. The results of the comparison show that dichloromethane is as efficient as, if not superior to, anhydrous ether on the Goldfish Extractor.

Dewey's work with the Goldfish Extractor was done with anhydrous ether on many samples of feeding stuffs, Taylor's on the four A.A.F.C.O. check samples with both fat solvents, and Hutchins' on cottonseed meal. A comparison shows that results obtained by the official method and by the three-hour Goldfish Extractor with ether are identical. Taylor, using both solvents, finds the differences are about the same as those with the

sixteen-hour extractor. Apparently, this short-time Goldfisch method gives excellent results.

#### RECOMMENDATIONS<sup>1</sup>

It is recommended—

- (1) That further study be given to dichloromethane as a fat solvent.
- (2) That a further study be made of the Goldfisch extraction apparatus.

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#### REPORT ON FAT IN DAIRY PRODUCTS USED AS FEEDS

By A. B. HEAGY (State Inspection and Regulatory Service, College Park, Md.), *Associate Referee*

In 1931 the Referee on Feeding Stuffs recommended that a committee be appointed to examine the A.O.A.C. methods and include, under the chapter Grain and Stock Feeds, all methods found in other chapters that might be applicable to the analysis of dried milk products used as feeding materials. This recommendation was not approved by the Committee on Recommendations of Referees, but it was suggested that collaborative work be done by an associate referee and that the recommendations be transmitted in the regular way.

The Associate Referee appointed in 1932 sent out to collaborators a sample of dried buttermilk to be examined by three methods: Roesse-Gottlieb (for dried milk), tentative under Dairy Products, p. 230, sec. 69; acid hydrolysis under Cereal Foods, p. 166, sec. 8; and Roesse-Gottlieb method (modified), as recommended by the American Dry Milk Institute of Chicago in 1929.

The modified method follows:

##### FAT IN DRIED MILK PRODUCTS

##### *Roesse-Gottlieb Method (modified)*

##### PROCEDURE

Weigh 1 gram of well-mixed milk powder and transfer immediately into a dry Mojonnier extraction flask or a dry Röhrig tube. Add 8.5 cc. of warm water, cork, and shake vigorously until dissolved, warming slightly if necessary to room temperature. Add 1.5 cc. of  $\text{NH}_4\text{OH}$  and shake thoroughly; add 10 cc. of 95% ethyl alcohol and shake thoroughly; add 25 cc. of ethyl ether, cork, and shake thoroughly; and finally add 25 cc. of petroleum ether and shake as before. Allow the ether layer to separate by leaving the flask or tube at rest for 20 minutes or until the upper liquid is practically clear. Draw off as much as possible of the ether fat solution in a flask or aluminum dish. Evaporate on the hot plate or steam bath at a temperature sufficient to allow complete evaporation, but not so high that spattering or vigorous boiling will result. To the residue in the flask or tube add 4 cc. of 95% ethyl alcohol and mix thoroughly without inserting the stopper. Add 15 cc. of ethyl ether and

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<sup>1</sup> For report of Subcommittee A and action of the Association, see *This Journal*, 17, 48 (1934).

shake thoroughly; add 15 cc. of petroleum ether and again shake thoroughly. Let stand and separate the ether layer as before, drawing it off into the same flask or dish and evaporating the ether.

Make a third extraction in exactly the same manner as the second, omitting the addition of alcohol. If necessary, carefully pour a few cc. of distilled water down the side of the tube to raise the level of the aqueous layer, so the ethers may be completely poured off. It is important that at no time any of the aqueous layer be allowed to run into the dish.

After the ether is entirely evaporated off place the dish in a Mojonnier oven for 5 minutes with the temperature at exactly 135° C., or in a boiling water oven for 30 minutes, or longer as required to bring it to constant weight.

Remove the fat completely with petroleum ether, and dry the residue; weigh, and deduct from the total weight. The loss in weight is the percentage of fat. Finally, correct this weight by a blank determination on the reagents used.

NOTES.—The time required for each shaking after the first portion of alcohol and subsequent additions of either ethyl or petroleum ether should be not less than 30 seconds, provided the shaking is very vigorous.

Each time after drawing off the ether layer the lip of the extraction flask or the spigot should be rinsed with petroleum ether, and the rinsings allowed to run into the aluminum dish.

The cork should be washed down at least once with petroleum ether.

Petroleum ether should have a boiling point below 60° C., and both petroleum and ethyl ether should be free from residue on evaporation.

The official method of the Association of Official Agricultural Chemists requires the use of a small quick-acting filter for drawing off the ether layer and washing the filter with petroleum ether. However, if care is used in making the separation, the use of the filter is not absolutely necessary.

TABLE 1.—*Collaborative results on fat in products used for animal feeding*

COLLABORATORS	ROESE-GOTTLIEB (MODIFIED)	ROESE-GOTTLIEB (TENTATIVE)	ACID HYDROLYSIS
	<i>per cent</i>	<i>per cent</i>	<i>per cent</i>
1	4.30	4.60	4.88
2	4.32	4.45	4.53
3	4.29	4.25	4.64
4	4.24	4.26	4.75
5	4.27	4.23	4.60
6	4.16	4.52	4.27
7	4.00	4.10	4.70
8	4.94	4.83	4.96
9	5.05	5.30	5.20
Average	4.40	4.50	4.74

Collaborator No. 9 heated the extractions from 1.5 to 100 hours. As this information was considered valuable, it is presented in Table 2.

The Roese-Gottlieb method (modified) gave the lowest results, but as a general average checked the Roese-Gottlieb (tentative) method by a tenth of one per cent. The hydrolysis method, in most cases, gave a

higher individual result, and an average result two-tenths higher than that for the Roese-Gottlieb (tentative).

TABLE 2.—*Results obtained by Collaborator No. 9*

HEATED	ROESE-GOTTLIEB (TENTATIVE)	ACID HYDROLYSIS	ROESE-GOTTLIEB (MODIFIED)
hours	per cent	per cent	per cent
1½	5.30	5.20	5.05
4	4.87	4.85	4.87
7	4.85	4.80	4.82
10	4.70	4.65	4.62
15	4.62	4.57	4.57
30	4.47	4.30	4.42
37	4.47	4.25	4.37
45	4.32	4.15	4.27
58	4.25	4.10	4.22
71	4.15	3.97	4.02
84	4.10	3.97	3.97
100	4.02	3.87	3.77

The Associate Referee found that in most cases the collaborators failed to discuss the merits or deficiencies of these methods.

#### COMMENTS

With the acid hydrolysis method it requires from 30 to 40 minutes to get the milk in solution by heating on a water bath. On transferring the solution to a Röhrig tube, there is a chance of losing some of the fat, as many small particles are left in the beaker. The evaporation of the ether extract on a steam bath seems questionable because of the possibility of absorbing moisture.

In the Roese-Gottlieb (tentative) method the time required to get the sample in solution by heating on a steam bath is too long. The transfer of the milk solution to the Röhrig tube makes possible the loss of some fat, as small crystals which do not dissolve on addition of the subsequent liquids are left in the beaker. The quantities of water, alcohol, and ammonium hydroxide required are too great for the size of the Röhrig tube from the bottom to the outlet, and necessitates the omission of the 4 cc. of alcohol for the second extraction.

The Roese-Gottlieb (modified) method is simpler and quicker, and it gives good comparative results.

#### RECOMMENDATIONS<sup>1</sup>

It is recommended that a more detailed study of this work be undertaken and that a report be given at the next meeting.

<sup>1</sup> For report of Subcommittee A and action of the Association, see *This Journal*, 17, 46 (1934).

## FIRST DAY

### MONDAY—AFTERNOON SESSION

The address of the president, which was delivered Monday afternoon, was published in *This Journal*, 17, 29 (1934).

No report on eggs and egg products was given by the referee.

No report on reducing sugars, sucrose, added salt, fat, lipoids,  $P_2O_5$  and crude albumin nitrogen was given by the associate referee.

No report on detection of decomposition was given by the associate referee.

No report on glycerol and unsaponifiable matter was given by the associate referee.

### REPORT ON PRESERVATIVES

By JOHN C. KRANTZ, JR. (State of Maryland Department of Health, Baltimore, Md.), *Referee*

The literature of the chemistry of foods is replete with researches concerned with the problem of preserving foods. Many of the old preservatives, such as formaldehyde and sulfites, can be identified by refined analytical methods. However, even a cursory survey of the subject will show that gradually, but certainly, the use of chemical substances as preservatives of foodstuffs is being discontinued in favor of the use of modern refrigeration and air-evacuated containers.

The 4th edition of the Swiss book on foodstuffs<sup>1</sup> presents qualitative methods for the identification of boric acid, hydrogen fluoride, sulfurous acid, sodium thiosulfate, potassium nitrate and hydrogen peroxide. Methods for the detection of salicylic, benzoic and cinnamic acids, as well as methods for their separation, are included. Of special interest is the inclusion of methods for the detection of para-hydroxybenzoic acid and its esters. It is now a matter of general information that during the last half decade many interesting data have been published regarding the efficacy of these compounds as disinfectants and preservatives. Various esters of the acid have been marketed under trade names, perhaps the best known of these being "Nipagin" and "Nipasol."

The use of alkali salts of ichthyolsulfonic acid as preservatives is of special interest. A British patent covers the use of alkali ichthyolsulfonates,

<sup>1</sup> Schweizerisches Lebensmittelbuch.



particularly the ammonium salt, in the preservation of apples, tomatoes, citrus and other fruits. The fruits are preserved by coating them with a gum solution containing a small percentage of the salt.

### EXPERIMENTAL

Last year the Referee reported that collaborative work had been begun on the quantitative determination of saccharin in drinks. The method studied was recommended by Gales and Pensa, who studied the method suggested by Giuseppi;<sup>1</sup> it depends upon the hydrolysis of saccharin into ammonia by evaporation in the presence of hydrochloric acid. Para-sulfonic benzoic acid does not form an imide and hence will not respond to the test. The resulting concentration of ammonium chloride solution is determined after nesslerizing by comparison with standard ammonium chloride solutions.

Certain minor modifications of the method were found to be necessary. Therefore the method, including these modifications, is presented, as are the results obtained by different collaborators.

### METHOD

Add 2 cc. of concentrated HCl to 50 cc. of the drink contained in a separatory funnel. Extract with two successive portions of ether, using 50 cc. for each extraction. Filter the ether extractions through cotton, and wash the combined extractions with approximately 5 cc. of distilled water to which has been added 1 drop of concentrated HCl.

Separate the ethereal layer and evaporate to dryness on a water bath. Add to the residue 5 cc. of water and 6 cc. of concentrated HCl and evaporate the solution to about 1 cc. on a hot plate with constant stirring. Again add 5 cc. of distilled water and 6 cc. of HCl and evaporate to about 1 cc. Dilute to 50 cc. with ammonia-free water and then dilute 5 cc. of this solution to 25 cc. with ammonia-free water. Add 2.5 cc. of Nessler's reagent and compare with ammonium chloride standards in the usual manner; 0.2923 gram of dry ammonium chloride is equivalent to 1 gram of saccharin, insoluble form, and to 1.39 gram of the sodium salt of the Pharmacopoeia crystallizing with two molecules of water of hydration. (For convenience an ammonium chloride standard equivalent to 200 parts per million of the insoluble form of saccharin is prepared.)

### Collaborative results

#### *Saccharin (soluble salt) in sarsaparilla (125 p.p.m.)*

COLLABORATOR	RECOVERY		PARENT
	p.p.m.	p.p.m.	p.p.m.
Margarethe Oakley	123	126	125
Edith Sollers	125	123	125
Helen Hawkins	122	122	125
Samuel Claman	120	120	125
William F. Reindollar	120	130	125
Referee	120	123	125

The method has been found satisfactory with other soft drinks. Vanillin, salicylic acid, and benzoic acid do not interfere with the quantitative determination of the saccharin.

In view of the results obtained it is recommended<sup>1</sup> that the method be adopted as tentative.

Associate Referee P. A. Clifford reports that during the course of a dried fruit survey for sulfur dioxide content, many samples of dried peaches and apricots were analyzed by the official method and also by the Monier-Williams tentative method. The results obtained by the official method were consistently lower than those obtained by the tentative method, sometimes as much as 300 p.p.m. of SO<sub>2</sub>. Gravimetric checks on the tentative method agreed very well with the titration figures. Clifford therefore recommends that during the coming year collaborative work be done on the Monier-Williams method with a view to making this now tentative method official and deleting the present official method.

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No report on sulfurous acid in dried fruits was given by the associate referee. See report of Referee on Preservatives.

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## REPORT ON COLORING MATTERS IN FOODS

By C. F. JABLONSKI (U. S. Food and Drug Administration, New York, N. Y.), *Referee*

Following the request of the Association, the Referee sent out to eight collaborators eight sets of three samples each of egg noodles. In order to have these samples comply closely with standard egg noodles a mixture was prepared containing 4 per cent of egg and a small quantity of coloring matter to make a product of normal appearance. The purpose of this experiment was to test the collaborator's ability to detect a trace of added color in the presence of a large quantity of egg material.

The samples were colored as follows:

*Sample A.*—Eggs—Tartrazine and orange I.

*Sample B.*—Eggs—Annatto.

*Sample C.*—Eggs—Yellow AB and yellow OB.

The reports submitted by the collaborators follow:

K. Breen, State of N.Y. Dept of Agriculture and Markets, Albany, N.Y.	Sample A.—Natural yellow pigment. Sample B.—Annatto. Sample C.—Yellow AB or yellow OB.
O. L. Evenson, Washington, D.C.	Sample A.—Tartrazine, only a trace of color.
S. S. Forrest, Washington, D.C.	Sample B.—Yellow AB or yellow OB.
J. A. Kime, Washington, D.C.	Sample C.—Yellow AB or yellow OB.
W. C. Woodfin, Savannah, Ga.	Sample A.—Egg yolk and naphthol—yellow S

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<sup>1</sup> For report of Subcommittee A and action of the Association, see *This Journal*, 17, 54 (1934).

Sample B.—Egg yolk and annatto.

Sample C.—Egg yolk and yellow OB.

C. D. Schiffman, New York City: Sample A.—Tartrazine and orange I.

Sample B.—Annatto.

Sample C.—Yellow AB or yellow OB.

The following criticisms and suggestions were offered by the collaborators.

*K. Breen.*—Use petroleum ether in place of ethyl ether.

*W. C. Woodfin.*—The test for lutein did not give satisfactory results. The strength of the alcoholic ferric chloride to be used might well be specified. It will be noted that none of the orange group was found in any of the samples. It might be well to specify the acidity with acetic acid to which the solution should be brought for this and previous ether extractions to yield the best results.

*C. D. Schiffman.*—I suggest that a small amount of alcohol be left in the extracted color mixtures in order to hold down the formation of emulsions in subsequent extractions.

It is evident that the collaborators did not experience any difficulties in separating and identifying yellow AB and yellow OB in Sample C.

#### DISCUSSION

Sample B, which contained annatto, was identified and reported correctly by all but one collaborator.

Sample A seems to have been the most difficult task. As stated, it was colored with tartrazine and orange I. However, only one collaborator reported both dyes. Tartrazine was reported by one, naphthol yellow S by another, while still another considered it a natural yellow pigment (eggs).

It is probable that the amyl alcohol extract of the orange I was almost colorless and therefore not considered by the collaborators. The difficulties in identifying the traces of tartrazine were increased by the presence of the soluble wheat color which masked the spot reactions. It is therefore advisable to insert into the method the necessary precautions, which would require more collaborative work.

The Referee also desires to state that progress has been made on the method of quantitative separation and estimation of mixtures of ponceau SX and ponceau 3R and of sunset yellow and tartrazine.

#### RECOMMENDATIONS<sup>1</sup>

It is recommended—

(1) That additional collaborative work be devoted to the separation and identification of coloring matters in macaroni products.

(2) That the study of the quantitative separation of ponceau SX and sunset yellow from the other permitted dyes be continued.

(3) That additional investigational work be devoted to the qualitative separation of light green SF yellowish, fast green FCF and brilliant blue FCF.

<sup>1</sup> For report of Subcommittee C and action of the Association, see *This Journal*, 17, 55 (1934).

## REPORT ON METALS IN FOODS

By H. J. WICHMANN (U. S. Food and Drug Administration, Washington, D. C.), *Referee*

The study of the determination of arsenic, copper, zinc, fluorine and lead in foods was undertaken by associate referees this year. The public health aspects of the spray residue problem have been reflected by an increased interest in analytical methods suitable for *control* work. Quite naturally this was followed by a desire on the part of manufacturers of food chemicals and of food ingredients to limit the lead, fluorine and like elements in their products to a safe minimum. Owing to its well-known toxic effects, lead occupied the leading place. In fact the demand for lead methods required the services of three or more analysts besides those of the associate and general referees. The results of their labors are summarized in a paper on lead methods, which will be published later.<sup>1</sup> The Referee will confine himself to general observations on the work of the several associate referees.

## ARSENIC

Last year the Association made the bromate method for the determination of arsenic in fresh fruits tentative, and recommended that its use be extended to vegetables and that a further study be made of interfering substances. The demand for quick and accurate lead methods suggested the advisability of changing the bromate method for arsenic so as to facilitate the determination of lead in the residue from the arsenic distillation. For this reason, the Associate Referee and others have used hydrazine sulfate as a reducing agent rather than complicate the lead method by the addition of interfering ferrous sulfate. Apparently the critical point in the modification is the volume of the distillation residue. When this becomes too low, sulfur dioxide is liberated, and it appears in the distillate, where it consumes bromate in the titration and causes high results. The Associate Referee used the increase in temperature as a guide for fixing this critical point and found the residual volume to be about 60 cc. In the Referee's own laboratory it was found that the residual volume should not be less than 50 cc. A mark at the 50 cc. volume should therefore be made on the digestion flask and the residual volume kept slightly above it.

The Associate Referee did not encounter any other interference from spray materials during the analysis of approximately 2500 samples of apples. He believes, however, that the bromate results should be checked by the Gutzeit method when large quantities of calcium are encountered, as in the analysis of some vegetables, apple chops, vinegar or apple jelly.

<sup>1</sup> *This Journal*, 17, 108 (1934).

He also finds that he can not always digest enough sample to obtain results on a pound basis without a sizeable factor, or always to yield 0.005 grain or 0.3 mg. of  $\text{As}_2\text{O}_3$ . Therefore, he recommends that the method be limited to materials from which such an amount can be obtained. The Referee concurs in this recommendation. He further recommends that the tentative method adopted last year be amended by deleting the use of ferrous sulfate as a reducing agent and substituting therefore hydrazine sulfate, mainly for its advantage in subsequent lead determinations. This will bring the bromate method for arsenic on fruits and vegetables into line with the determination of arsenic in insecticides. The Referee believes there is no necessity for further work on the bromate method in connection with fruits and vegetables and the use of this method on products of very different nature is not recommended at this time.

C. R. Gross<sup>1</sup> contributed a paper last year on the interference of nicotine and incomplete reduction of arsenates under some circumstances, both causing low results. He was appointed associate referee to study further (1) the problem of interferences in the Gutzeit method and (2) the conditions of reduction and the lengthening of the range of the determination. The Referee also hoped to get a report on the arsine distillation method with the use of the newly available electrolytic zinc. Routine work on spray residues, however, interfered.

The Referee believes that at the present time the accuracy of the lead determination in spray residues is actually better than that of arsenic by the Gutzeit method and that therefore it is a particularly propitious moment to make greater effort to improve the arsenic methods. Therefore, he believes that the recommendations of last year with reference to the Gutzeit and arsine distillations should be repeated.

#### COPPER AND ZINC

It was recommended last year that a study be made of micro methods for copper up to 1 mg. quantities, preferably by colorimetric methods, and of zinc by macro and micro methods with the dividing line set at 2 mg. No report was received from the Associate Referee, therefore the Referee repeats his recommendation of last year. In addition, he wishes to point out that the Germans, under the leadership of Hellmut Fischer,<sup>2</sup> are making progress in the micro determination of metals with the help of the new reagent, diphenylthiocarbazone, "dithizone" for short. This reagent is rather scarce in this country at present, but some universities and commercial houses have prepared it for their own use and can supply it in small quantities. It appears that under special conditions this reagent is almost a specific for certain metals, copper among them. It is recommended that the next associate referee look into the possibilities of this reagent for the determination of copper.

<sup>1</sup> *This Journal*, 16, 398 (1933).

<sup>2</sup> *Wiss. Veröffentlich. Siemens Konzern*, 12, 44 (1933); *Z. angew. Chem.*, 46, 442 (1933).

## FLUORINE

Last year at the symposium three members of this Association reported their work on the determination of fluorine. This work will soon be published.<sup>1</sup> This year many methods have been published demonstrating the great interest this element has aroused in biochemical, toxicological, public health and regulatory circles. Most of the newer methods are concerned with the determination of fluorine in water supplies, but this determination is a simpler problem than that of determining it in toxicological and biological material or in foods. Therefore the Referees believed it advisable to restrict the first collaborative work to water. As all the fluorine methods are comparatively new, individual analysts have probably not had experience with more than one method. It was believed fairer to send identical samples to each collaborator and let him select his own method. The work this year, therefore, might become an elimination contest to "shake down" the methods for next year.

The Associate Referee's report does not describe the details of the various methods used, but refers the interested reader to the literature. The original papers discuss more or less in detail the interferences and the way they are eliminated or their effects evaluated. The composition of the waters sent out to collaborators was such as to constitute a severe test of the methods with respect to such interfering substances as may be found in waters. Of course, interfering elements found in foods or other biological material, but not in water, were not involved. In general, the results appear to be as good as could possibly be expected. There appear to be at least three methods of great promise. The Referee, therefore, concurs in the recommendation that next year the work on fluorine be continued with special reference to preparatory treatment of organic material and determination of the fluorine by one or all of the methods tried this year.

## LEAD

General interest in the determination of lead has been greater this year than at any time since 1925-26, the years of the tetra-ethyl lead investigations. The Referee's interest was mainly in the problem of spray residues. This problem was attacked by two independent groups, the Virginia Department of Agriculture under the leadership of Catesby Jones and the U. S. Department of Agriculture represented by the Associate Referee on Lead and the Referee on Metals in Food. The results of these labors are to be given at the symposium tomorrow.<sup>2</sup> At this time, therefore, there is no necessity for an associate referee's report. The Referee desires to make some general observations and to indicate the direction that future efforts with respect to tentative or official methods will probably take.

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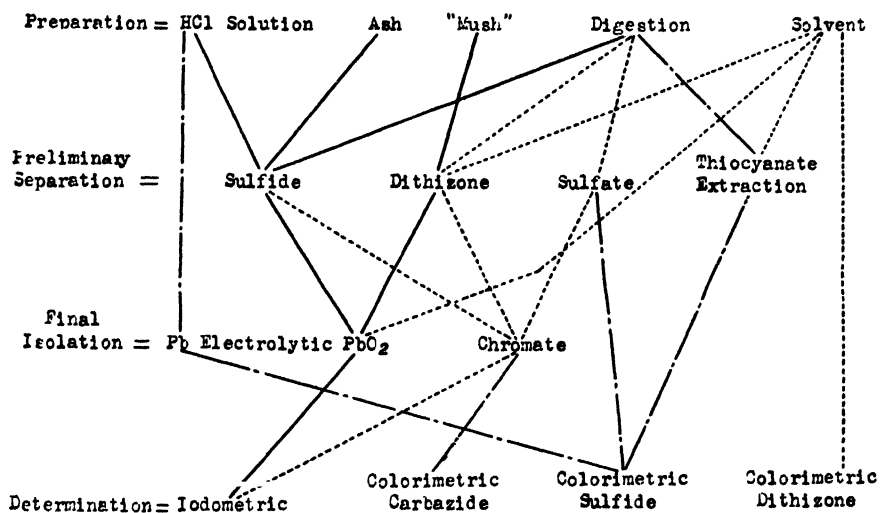
<sup>1</sup> *This Journal*, 16, 612, 619 (1933); *Ind. Eng. Chem. Anal. Ed.*, 5, 7 (1932).

<sup>2</sup> *This Journal*, 17, 108, 141 (1934).

The Referee was not in favor of extensive collaborative work this year. About all that could be done was to get some new methods ready for trial and to give the analysts who would be expected to cooperate a year's experience.

The Referee has abandoned the hope that one method can be found so superior to all others that it can be made the sole official method for the determination of lead in all food or biological material. The lead content, the size of sample that can be handled, and the nature of the material vary so widely that it is hopeless to try to simmer the many possibilities down to one procedure. Each analyst should have some choice in the matter of preliminary separation, isolation and final determination to fit his own particular problem. If the interferences, limits of accuracy, etc., are clearly indicated, he should be able to chart his course with confidence.

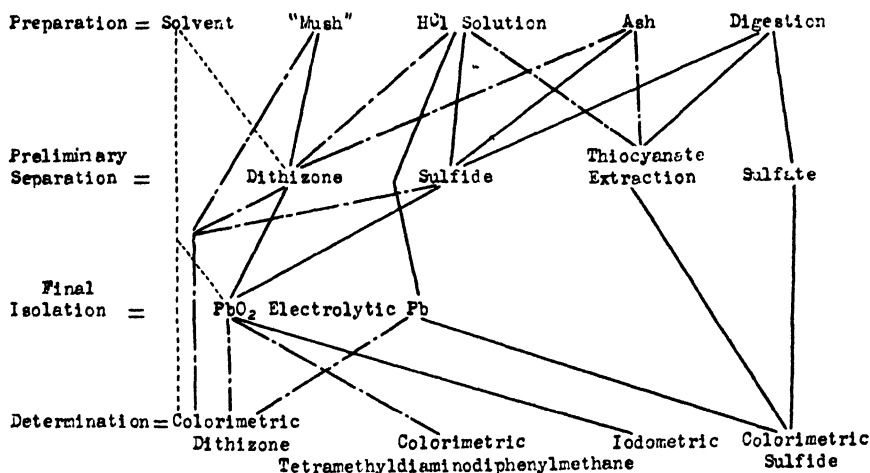
#### PRESENT METHODS



There remains, however, the question as to which method or methods should be studied collaboratively with a view to adoption as tentative or official. The ultimate method will probably be a combination of several methods with alternative intermediate steps to fit various kinds of products. To prophesy what the future may bring requires a good comprehension of the present state of affairs. Therefore, the Referee has prepared a chart or flow sheet (Fig. 1) illustrating the differences in preparation of sample and the preliminary separation, isolation, and determination of lead by present methods. It shows in solid lines the steps in the methods that have been investigated and that are believed by the Referee and his associates to be sound. The dotted lines illustrate the methods investi-

gated but not especially favored by him and the rapid or approximate methods found useful and practicable in the field but perhaps not suitable for official use. The methods investigated and recommended by others are given by broken lines. The interferences, difficulties, or limitations that make one method preferable over another are not shown. However, the many starting points, varying with the nature of the material, and the many ways of arriving at the desired end, are indicated. The Referee could lengthen this report by considering the advantages and shortcomings of the many possible permutations, but in view of the paper in process of preparation, he will merely present Fig. 2, which illustrates his idea of what the lead method or methods of the future may be. The solid lines indicate the steps in the methods that merit serious consideration by the

#### PROSPECTIVE METHODS



Association. The dotted lines show the paths of rapid methods, and the broken lines indicate possible new modifications as yet untried. Fig. 2 differs from Fig. 1 in two general aspects: (1) The elimination of the chromate methods; and (2) the greatly increased use of H. Fischer's<sup>1</sup> new reagent, dithizone. These two trends should receive the close attention of the Association.

#### RECOMMENDATIONS<sup>2</sup>

It is recommended—

- (1) That the bromate method for arsenic, made tentative last year, be amended by substituting hydrazine sulfate for ferrous sulfate for reduction purposes so as to facilitate the determination of lead in the residue.

<sup>1</sup> *Loc. cit.*

<sup>2</sup> For report of Subcommittee C and action of the Association, see *This Journal*, 17, 55 (1934).



(2) That the bromate method be restricted to the determination of arsenic in fruits or vegetables, samples of which containing at least 0.005 grain or 0.3 mg. of  $As_2O_3$  can be digested.

(3) That no further work be done on the bromate method for the determination of arsenic in fruit and vegetables.

(4) That the recommendation of last year that work be done on improvements and interferences of the Gutzeit method and the arsine distillation method for arsenic be repeated.

(5) That the recommendation of last year that more work be done on colorimetric methods for quantities of copper up to 1 mg. and macro and micro quantities of zinc with the dividing line at approximately 2 mg. be repeated.

(6) That the fluorine work be continued, especially with respect to the preparatory treatment of organic material and the determination of the fluorine by one or all of the methods tried this year.

(7) That a collaborative study of lead methods, leading to the adoption of official methods, be begun.

## REPORT ON BROMATE METHOD FOR DETERMINATION OF ARSENIC IN FOODS

By W. CATESBY JONES (Department of Agriculture, Richmond, Virginia), *Associate Referee*

In order that the residue from the bromate method for the determination of arsenic might be used for the determination of lead, the distillation of  $AsCl_3$  was changed to use hydrazine sulfate instead of ferrous sulfate. This change makes the removal of oxides of nitrogen easier as small quantities of  $NO_2$  do not interfere when hydrazine sulfate is used in the distillation. The following changes, therefore, were made in the bromate method published in *This Journal*, 16, 75 (1933):

### CHANGES IN REAGENTS

Reagents (e) and (f) were deleted, and in their place the following was substituted: *Hydrazine sulfate-sodium bromide soln.*—Dissolve 20 g. of hydrazine sulfate and 20 g. of NaBr in 1 liter of HCl (1+4).

### CHANGES IN PROCEDURE

The paragraph entitled "Removal of Oxides of Nitrogen" was changed to read: "After digestion is complete, add 50 ml. of distilled  $H_2O$  and 25 ml. of reagent (d) and boil until white  $SO_2$  fumes extend well up into the neck of the flask. If the burners used are not hot enough to drive the fumes well up into the neck of the flask, omit the use of reagent (d). (If  $SO_2$  fumes are not driven well up into the neck of the flask some of the decomposition products of the oxalate and urea soln may be left in the sample and produce an interference when titrated with the bromate soln.)

The paragraph entitled "Distillation of  $\text{AsCl}_3$ ," was changed to read: Add 25 ml. of  $\text{H}_2\text{O}$  to the digested soln in the Kjeldahl flask and cool to room temperature. Put 100 ml. of  $\text{H}_2\text{O}$  into the Erlenmeyer flask. Add to the soln in the Kjeldahl flask 20 g. of  $\text{NaCl}$  and 25 ml. of hydrazine sulfate-sodium bromide soln and connect the distilling tube. Heat the Kjeldahl flask over a small well-protected flame, and distil into the  $\text{H}_2\text{O}$  in the Erlenmeyer flask. (The heating is not intended to boil the soln but to bring about the evolution of the  $\text{HCl}$  gas, which carries over the  $\text{AsCl}_3$  with it. The absorption of the evolved  $\text{HCl}$  gas by the water causes a rise in temp. which furnishes an indication of the progress of the distillation.) Adjust the flames so that the temp. of the distillate soln will rise to  $90^\circ$  in 9-11 min., at which temp. distillation is complete.

### INTERFERENCES

The possibility and extent of interference from sulfur dioxide fumes during distillation was investigated. No interference was noted when the procedure outlined was carried out, that is, to continue the distillation until 100 cc. of water in the receiving flask is raised to  $90^\circ\text{C}$ ., this being accomplished in not more than 11 minutes. A large number of blanks were run in this way, with no irregularities, all being between 0.3 and 0.4 cc. of bromate soln. Also a large number of standards were run with large quantities of arsenic present, some as high as 0.1 grain, and all the results showed practically 100 per cent recovery. However, if the distillation proceeds further, as in cases when the water in the receiving flask is cooled, or if a much larger quantity of sulfuric acid is used than called for in the method the blanks will be too high. The temperature of the water in the receiving flask furnishes a good indication of the progress of the distillation. Thirty samples were picked at random from routine analysis and the residues after distillation were measured. The average was 58 cc.  $\pm$  3 cc.

No interference from spray materials has been encountered in the analysis of approximately 2500 samples of apples by the Division of Chemistry, Department of Agriculture of Virginia, in the current season.

### APPLICABILITY OF METHOD TO MATERIALS OTHER THAN APPLES, PEARS AND OTHER FRESH FRUITS

In most cases the method gives good results when used to determine arsenic on celery, cabbage, apple chops, vinegar and apple jelly. However, the results are not always consistent, especially in materials containing large quantities of calcium. The calcium may occlude small quantities of  $\text{NO}$  or  $\text{NO}_2$ . Good results cannot be obtained with apple pomace or stock feeds unless a large quantity (200 cc.) of water is used to dispel the oxides of nitrogen. Added to this is the fact that with materials of this kind only  $1/4$  or  $1/8$  of a pound can be digested satisfactorily, which makes it necessary to multiply any error obtained by either 4 or 8 to bring the result to a pound basis.

Therefore, in work with materials of this kind it is thought best not

to accept the bromate result as final but to check it by a Gutzeit determination on the distillate, which can be run before or after titration. Better Gutzeit results can usually be obtained after a distillation of the arsenic, as in the bromate method. Therefore it was thought best to apply the bromate method (as stated last year) only to materials of which it is practicable to digest a sample sufficient to yield 0.005 grain of  $\text{As}_2\text{O}_3$ .

No report on the arsine distillation and Gutzeit methods was given by the associate referee.

No report on copper and zinc was given by the associate referee.

## REPORT ON FLUORINE IN FOODS

By DAN DAHLE (U. S. Food and Drug Administration, Washington, D. C.), *Associate Referee*

In order to get an idea of the suitability of some of the recently published methods for the determination of small quantities of fluorine the Associate Referee distributed for collaborative analysis two samples of artificially prepared waters to which known quantities of fluorine had been added. The approximate composition of these waters, which were prepared from distilled water and c. p. chemicals, is shown in Table 1.

TABLE 1.—*Composition of samples*

	SAMPLE A		SAMPLE B	
	APPROX.	FOUND*	APPROX.	FOUND*
	p.p.m.	p.p.m.	p.p.m.	p.p.m.
Ca	146	172	215	218
Mg	78	95	39	48
Cl	2180	2210	64	59
$\text{SO}_4$	907	947	3316	3330
$\text{HCO}_3$	590	523	328	260
Tannic acid	—	—	4	—

\* Analysis reported by Miss Foster, U. S. Geological Survey.

Samples of 500 cc. each (A and B) were made alkaline, evaporated, and distilled with sulfuric acid according to the procedure of Willard and Winter.<sup>1</sup> The fluorine content was then determined by the Steiger method as modified by H. J. Wichmann and the writer. The following results were obtained: A, 0.08 p.p.m.; B, 0.05 p.p.m.

<sup>1</sup> *Ind. Eng. Chem. Anal. Ed.*, 5, 7 (1933).

TABLE 2.—*Collaborative results*

ANALYST NUMBER	SAMPLE	WILLARD AND WINTER METHOD		AV.		FOSTER METHOD		AV.		MODIFIED STUBBER METHOD		AV.	
		FLUORENCE TITRATION WITH ER- CONIUM-ALIZARINE LAKE OR ALIZARINE SULFONATE INDICATOR		A	B	COLORIMETRIC—BLEACHING AC- TION OF F ON FERRIC THIO- CYANATE		A	B	COLORIMETRIC—BLEACHING AC- TION OF F ON PEROXIDIZED TITANIUM		A	B
1	A	1.9, 2.3		2.1				—	—			—	—
	B	4.0, 4.2, 4.5			4.3			—	—			—	—
2	A	2.7		2.7		2.0, 2.4, 2.5		2.3	—			—	—
	B	2.7, 3.0, 3.9, 4.2			3.5	2.4, 2.5, 2.6			2.5			—	—
3	A			—	—	1.80, 1.70		1.8	4.5			—	—
	B			—	—	4.4, 4.5						—	—
(1) (2) 4	A			—	—			—	—	2.0, 2.0		2.0	4.3
	B			—	—					4.0, 4.0, 4.0, 5.0			
(1) (3) 5	A			—	—			—	—	1.5		1.5	4.0
	B			—	—			—	—	4.0			
(1) (3) 6	A			—	—			—	—	1.5		1.5	4.0
	B			—	—			—	—	4.0			
(3) (4) 7	A	2.1, 2.3, 2.2		2.2				—	—	2.1, 2.3, 2.3, 2.0		2.2	4.0
	B	4.4, 4.2, 4.3			4.3			—	—	3.9, 3.8, 3.9, 4.2			
8	A	2.64, 2.55, 2.42		2.5				—	—			—	—
	B	4.39, 4.63, 4.31, 4.55			4.5			—	—			—	—

(1) Nessler tubes used for color comparison.

(2) Sample A: Distillate colored yellow. Strong odor of chlorine. With 40 cc aliquot used for color comparison a green shade resulted, differing from that of standards and giving a result of 0.5 p.p.m.

(3) Determination made on 10 cc. sample direct, without previous distillation showed:  
Sample A  
Analyst  
p.p.m.  
5 1.5  
6 1.5  
7 3.0  
8 3.4

(4) Polarizing photometer used for color measurements.

To 17.5 liters of each of these waters there was added to A, 35 cc. and to B, 70 cc. of a standard sodium fluoride solution, 1 cc. = 1 mg. of F. This gave a fluorine content as follows:

<i>Added</i>		<i>Total (added and blank)</i>	
	<i>p.p.m.</i>		<i>p.p.m.</i>
A	2.0		2.08
B	3.98		4.03

Each collaborator was asked to use either the Willard and Winter,<sup>1</sup> the Foster,<sup>2</sup> or the modified Steiger method,<sup>3</sup> and any other method or modification desired. The analysts reporting were M. D. Foster, O. B. Winter, R. U. Bonnar, C. S. Boruff, H. V. Smith, J. B. Snider, W. C. Woodfin and the Referee. The results are shown in Table 2.

### CONCLUSIONS

(1) Each of the three methods investigated can give reasonably accurate results.

(2) In the Foster method, where no isolation of fluorine precedes the determination, there appears to be a danger of variations when the salt concentration is high, due to the application of corrections that depend on the accuracy of other analyses.

(3) In the modified Steiger method, when used with Nessler tubes, care must be taken in the presence of chlorides. Either the addition of potassium permanganate must be omitted during the distillation or the aliquot used for final color comparison must be so small that the color of free chlorine will not interfere.

### RECOMMENDATIONS\*

It is recommended—

- (1) That the work on fluorine be continued.
- (2) That stress be laid on methods for bringing the fluorine into solution, particularly where it is found with large quantities of organic materials.

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No report on lead was given by the associate referee.

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### REPORT ON FRUITS AND FRUIT PRODUCTS

By B. G. HARTMANN (U. S. Food and Drug Administration, Washington, D. C.), *Referee*

No formal reports were received from the Associate Referees on Soluble Solids, Ash and Effect of H-ion Concentration on Extraction of Fruits.

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<sup>1</sup> *Loc. cit.*

<sup>2</sup> *Ind. Eng. Chem. Anal. Ed.*, 5, 234 (1933).

<sup>3</sup> *This Journal*, 16, 612 (1933).

\* For report of Subcommittee C and action of the Association, see *This Journal*, 17, 55 (1934).

Reports on Moisture in Dried Fruits and Fruit Acids will be presented.

The Referee recommends discontinuance of the subjects of ash and H-ion concentration.

Last year Tilden and Salinger submitted a joint report on the determination of iron and aluminum, but owing to the apparent incompleteness of the work in several of its phases, it was not presented at the meeting. In view of the recommendation that this work be discontinued, however, it is believed desirable to submit the report at this time in order that a record may be had of the work done thus far. (See. p. 208.)

McRoberts, Associate Referee on Soluble Solids, performed sufficient experimental work to show that for the determination of soluble solids by means of the refractive index, the Schönrock table for sucrose is not applicable without correction in the case of products high in invert sugar, such as jellies. He found that as the quantity of invert sugar increases, the necessity for correction becomes more apparent. In case of a jelly the error may amount to 1.5 per cent or more. McRoberts recommends a study of the refractive values of invert sugar, dextrose, and organic acids, and also of mixtures of these with sucrose, for the purpose of fixing the necessary corrections to be applied when the Schönrock table is used. The Referee is impressed with the importance of the work and concurs in the recommendations made.

The report on the determination of moisture in dried fruits by Clifford is a comprehensive discussion of the various factors involved. It is replete with valuable information concerning the drying of fruits, but its diversified nature makes it inadvisable to review each detail in the space allotted here. Briefly, it is demonstrated experimentally, in the case of dried fruits, that 6 hours' drying in vacuo at 70°C. is as satisfactory as is the 12 hour drying period prescribed by the official method. Clifford also points out that certain precautions must be observed in order to assure reliable results. This is particularly necessary with regard to the drying temperature. He has found that a deviation of  $\pm 1^\circ$  from 70°C. will result in an error of approximately 0.1 per cent moisture. Based upon the results obtained, Clifford makes a number of recommendations in which the Referee concurs.

On the subject of Fruit Acids time was devoted to the collaborative study of the method for the determination of malic acid described by Hartmann and Hillig<sup>1</sup> With the exception of the results of one collaborator, the work proved satisfactory. Hillig analyzed 29 fruits and 29 vegetables for citric, malic, and tartaric acids by the A.O.A.C.<sup>2</sup> methods. In addition to this work the citric acid method was applied to the analysis of oysters, cacao, coffee, malt, the germ and bran of the wheat berry, milk, and milk bread. Of six varieties of apples examined for citric acid—Jona-

<sup>1</sup> *This Journal*, 15, 848 (1932).

<sup>2</sup> *Ibid.*; *Methods of Analysis*, 1930, 272, 273.

than, McIntosh, Rome Beauty, Delicious, Grimes Golden, and Yellow Transparent—only the last-mentioned variety was found to contain the acid. No trouble was experienced with the method in the examination of any one of the materials mentioned.

Considerable time was devoted to the study of methods for the determination of lactic acid in fruit products. It is believed that the subject will be completed next year. Further study on the subject is recommended.

C. S. Ladd, Food Commissioner and Chemist of North Dakota, reports that in his experience the official method for the determination of pectic acid in fruit gives low results. He believes that the method could be advantageously modified by directing that in the preparation of the solution a small amount of ammonium oxalate be added before boiling. He further suggests the study of electrometric methods for titrating fruits and fruit products. The Referee believes that the points raised should receive consideration by the Association, and recommends<sup>1</sup> that associate referees on the subjects be appointed.

No report on soluble solids was given by the associate referee. See report of the Referee on Fruits and Fruit Products.

No report on ash was given by the associate referee. The following report, held over from last year, is presented instead. See report of the Referee on Fruits and Fruit Products.

## REPORT ON ASH (IRON AND ALUMINUM CONSTITUENTS)

By L. A. SALINGER and D. H. TILDEN<sup>2</sup> (U. S. Food and Drug Administration, San Francisco, Calif.), *Associate Referee*

In the 1931 report it was recommended that further work be done on the determination of iron and aluminum. The Associate Referee suggested that with a carefully controlled pH, in a solution containing excess phosphate and an alkaline buffer, such as sodium or ammonium acetate and thymol blue, it might be possible to separate iron from aluminum. He favored cooling the solution containing the combined precipitate of iron and aluminum phosphate to room temperature, then filtering and washing with a cold solution containing a volatile electrolyte adjusted to a suitable pH.

In the beginning of the experimental work it was found that when the hot solution containing the combined iron and aluminum phosphates was

<sup>1</sup> For report of Subcommittee C and action of the Association, see *This Journal*, 17, 55 (1934).

<sup>2</sup> Presented in 1932, but held for publication later. See report of the General Referee on Fruits and Fruit Products.

filtered, and the precipitate washed in the cold with a solution of an electrolyte of suitable  $pH$  a very unsatisfactory condition resulted. The precipitate was slow to filter and difficult to wash and the process was time-consuming. Hillebrand and Lundell<sup>1</sup> state that aluminum phosphate may be washed with hot water, or a hot 5 per cent solution of ammonium nitrate. There is, also, the question of the hydrolysis of the ferric phosphate, as well as of the aluminum phosphate, when filtered and washed hot.

Numerous experiments were run with known amounts of pure aluminum and iron, in separate solutions, both with hot and cold treatment. The elements were precipitated as the phosphate from a hydrochloric acid solution, at a  $pH$  of 4.0, determined colorimetrically. (Bromcresol green indicator was used throughout for this  $pH$  range.) In one case they were allowed to stand until cool, then filtered and washed with a cold solution containing 0.1 per cent ammonium acetate, adjusted to a  $pH$  of 4 with acetic acid. This low concentration was finally decided upon, because it gave entirely satisfactory results as a non-hydrolyzing wash and did not interfere with subsequent ashing as did more concentrated solutions. In the other case the precipitated phosphate was filtered from the hot solution, washed with the same wash solution, hot, and in both cases the precipitate was dried, ignited, weighed, and calculated as the oxide. The washing was continued till the filtrate gave no test for chlorides, and a control was run on all reagents. The results are given in Table 1.

The data given in Table 1 indicate that in regard to accuracy there is no choice between hot and cold treatment; as hot treatment is more easily handled, however, it was followed in all subsequent work.

In an attempt to obtain quantitative recoveries of iron from aluminum, experiments were conducted to determine the possibilities of separating them by carefully controlling the  $pH$ . Results indicated that this could not be done with any degree of satisfaction because there is apparently no clean-cut end point. Ferric phosphate begins to precipitate at a  $pH$  of approximately 2.0. When the solution containing the mixed phosphates is adjusted to a  $pH$  of 2.1 to 2.3, boiled, then allowed to cool before filtering, a low result for iron is obtained. Table 2 shows the successive recoveries of iron phosphate with increasing  $pH$  values. If, however, the precipitate is filtered hot and washed hot, a much better recovery is obtained at a lower  $pH$ . Iron alone begins to precipitate under 2.0 and appears to precipitate completely at a  $pH$  of 3.0–3.2, when filtered hot. Aluminum phosphate does not come down in the cold at a  $pH$  of 2.8, but comes down heavily at this  $pH$  when heated. There is a slight precipitate from hot solutions at  $pH$  as low as 2.2. These results are given in Table 2.

It was also found that there is a very definite relationship between the temperature and  $pH$  value in the precipitation of calcium as the phos-

<sup>1</sup> Applied Inorganic Analysis, p. 399.



TABLE 1.—*Comparisons of hot and cold treatment of iron and aluminum precipitated as phosphates and weighed as oxides*

TREATMENT	QUANTITY RECOVERED			
	FROM MAIN SOLUTION	FROM FILTRATE FROM MAIN SOLN.	FROM WASHINGS	TOTAL
	mg.	mg.	mg.	mg.
$\text{Al}_2\text{O}_3$ (24.5 mg. present)				
Filtered and	24.8	0.1	0.0	24.9
washed in cold (pH 4)	23.7	0.5	0.6	24.8
	23.8	0.4	0.8	25.0
	23.6	0.9	0.6	25.1
	24.0	0.8	0.0	25.3
	24.8	0.0	0.0	24.8
	24.6			24.6
	24.7			24.7
	25.1			25.1
Ditto, except pH slightly increased (4+)	24.6	0.0	0.7	25.3
	24.7	0.1	0.6	25.4
Filtered and	24.3	0.2	not det.	24.5
washed, hot	23.9	0.3	not det.	24.2
	25.1	0.1	0.0	25.2
	24.7			24.7
	24.6			24.6
	25.1			25.1
$\text{Fe}_2\text{O}_3$ (26.0 mg. present)				
Filtered and	25.9		0.3	26.2
washed in cold (pH 4)	26.1			26.1
	26.2			26.2
Filtered and	26.7			26.7
washed hot	26.0			26.0
	25.8			25.8

phate. In the cold, a solution containing 50 mg. of calcium and 120 mg. of disodium phosphate in about 250 cc., began to precipitate slightly at a pH of 6.5. On boiling a heavy precipitate came down. Hydrochloric acid was added until the solution was clear (pH 3.2) and sodium acetate was added to adjust the pH to 3.6. A slight turbidity occurred on heating, and at pH 4.7–4.8 a heavy deposit came down.

Table 3 shows the effect of pH on the precipitation of varying quantities of calcium, with and without heat. It is apparent that small amounts of calcium (50 mg.), will not interfere with the hot precipitation of the phosphates (iron and aluminum) under a pH of 4.3. With 100 mg. present, calcium phosphate precipitates at a pH of 3.4–3.5 from hot solutions and with 150 mg. present it will come down at 3.0–3.2. It is advisable, there-

fore, to make a reprecipitation of iron and aluminum in all cases where the calcium content exceeds 50 mg.

TABLE 2.—*Recoveries of iron from aluminum*  
(250 cc. soln.; 3 cc. 10%  $\text{NaH}_2\text{PO}_4$ . Ammonium Acetate, pH 4, for washing.)

TREATMENT	RECOVERIES (MG.)				RECOVERY FROM WASH SOLN. pH4	TOTAL RECOVERY
	pH 2.1-2.3	2.8-3.6	3.6-4.0	4		
<i>Fe<sub>2</sub>O<sub>3</sub> present, 26.0 mg.</i>	<i>per cent</i>	<i>per cent</i>	<i>per cent</i>	<i>per cent</i>	<i>per cent</i>	<i>per cent</i>
Cold	23.8	1.3	0.9		0.3	26.2
Hot	23.7	2.5	0.0		0.4	26.6
<i>Al<sub>2</sub>O<sub>3</sub> present, 24.5 mg.</i>						
Cold			3.4	24.8	0.1	24.9
				23.7	2.6	26.3
			23.7	1.1	0.1	24.9
Hot				25.1	0.1	25.2
				25.1	0.0	25.1

TABLE 3.—*Precipitation of large and small quantities of calcium as phosphate at varying pH values*

CaO PRESENT	pH AT WHICH NO PFN. OCCURS IN COLD	pH AT WHICH PFN. OCCURS ON BOILING
<i>mg.</i>		
50	6.5	4.7
	4.5	4.5
	4.2	4.4
	3.8	4.3
100	3.8	3.8-4.0
	3.5	3.6-3.8
	3.3	3.6
	3.2	3.4-3.5
150	3.3-3.6	3.7-4.1
	3.3-3.5	3.6-4.1
	3.0-3.2	
	3.0	
	3.0	
		3.0-3.2

The results in Table 3 indicate that very little iron phosphate is lost in the actual washing process, but in order to determine if any material change occurred in the chemical composition of the precipitated phosphate due to washing, a few experiments were made. In these, the pure

iron was thrown down and weighed as phosphate, calculated to  $\text{Fe}_2\text{O}_3$ , dissolved, iron determined by precipitation with cupferron and  $\text{P}_2\text{O}_5$  determined by the official method. These results, when compared with the theoretical, show that possibly the iron phosphate contains a slight excess of  $\text{P}_2\text{O}_5$ , but any hydrolysis that occurs is believed to be so small that it may be disregarded for all practical purposes. The results given in Table 4 are for iron and  $\text{P}_2\text{O}_5$  determined on different aliquots of the original iron solution.

TABLE 4.—*Recovery of iron and  $\text{P}_2\text{O}_5$  from precipitated ferric phosphate*  
(Pure iron wire used.  $\text{Fe}_2\text{O}_3$  calc., 26.0 mg.)

WEIGHED AS $\text{FePO}_4$	CALC. TO $\text{Fe}_2\text{O}_3$	PPT. WITH CUPFERRON WEIGHED AS $\text{Fe}_2\text{O}_3$	THEORETICAL $\text{P}_2\text{O}_5$ CALC. FROM WGT. OF PHOSPHATE	$\text{P}_2\text{O}_5$ DETERMINED ON IGNITED PPT.	WASH SOLUTION
gram	mg.	mg	mg.	mg.	
0.0499	26.4	26.5	23.5	—	Amm. Acetate, hot
0.0495	26.2	26.3	23.3	—	Amm. Acetate, hot
0.0501	26.5	—	23.6	{ 24.00 24.00	Amm. Acetate, hot
0.0494	26.1	—	23.3	{ 23.7 23.7	Amm. Acetate, hot
0.0499	26.4		23.5		Amm. Nitrate, hot
0.0498	26.3		23.4		Amm. Nitrate, hot
0.0500	26.4		23.5		Amm. Nitrate, hot
0.0502	26.5		23.6		Amm. Nitrate, hot
0.0502	26.5		23.6		Amm. Nitrate, cold
0.0499	26.4		23.5		Amm. Nitrate, cold

Owing to the fact that iron and aluminum may be precipitated quantitatively as phosphates, it seemed best to weigh the mixed phosphates and determine iron by the cupferron method and the aluminum by difference. The ignited mixed phosphates are more easily soluble in hydrochloric acid than in sulfuric acid, so are dissolved in hydrochloric acid, evaporated to dryness, taken up in sulfuric acid, and the iron is precipitated by cupferron. This procedure, rather than fusion, is necessary to remove the possibility of nonvolatile salts being occluded with the iron.

If the analyst desires to make a separate quantitative determination of aluminum the filtrate from the cupferron precipitate may be used and aluminum determined as the phosphate. Or it may be more desirable, particularly with larger amounts of aluminum, to use the procedure for aluminum as a direct method. In this case evaporate the filtrate from the cupferron precipitation of iron with nitric acid until organic matter is destroyed and remove all nitric acid, as it interferes with the indicator later. Use bromcresol green and adjust to a pH of approximately 3.2 with concentrated ammonium hydroxide. Add an excess of sodium monophos-

phate and sodium acetate. Filter, wash, ignite and weigh as aluminum phosphate.

Table 5 shows results obtained by determining iron by cupferron, and aluminum as phosphate with calcium present. The calcium was separated according to the present official method.

TABLE 5.—*Determination of iron and aluminum with calcium present*

Fe as $\text{Fe}_2\text{O}_3$ (mg.)		Al as $\text{Al}_2\text{O}_3$ (mg.)		CALCIUM as $\text{CaO}$ (mg.)	
PRESENT	RECOVERED	PRESENT	RECOVERED	PRESENT	RECOVERED
26.0	25.8				
		24.5	23.7		
		24.5	24.2		
26.0	26.3	24.5	24.0	25.0	24.3
10.4	10.5	9.8	10.0	25.0	25.0
10.4	10.3	9.8	9.8	50.0	50.8

An artificial ash solution was prepared and analyzed by the proposed method for iron and aluminum and the official method for the other ash constituents. Potash and phosphates were present but not determined. Results are given in Table 6.

TABLE 6.—*Analysis of a known ash solution*

$\text{Fe}_2\text{O}_3$		$\text{Al}_2\text{O}_3$		$\text{Mg}_2\text{O}_3$		$\text{CaO}$		$\text{MgO}$	
PRES.	REC.	PRES.	REC.	PRES.	REC.	PRES.	REC.	PRES.	REC.
mg.		mg.		mg.		mg.		mg.	
26.0	25.57	24.5	23.7	10.3	10.3	50.0	51.0	25.0	26.0
26.0	25.30	24.5	23.7	10.3	10.4	50.0	49.8	25.0	26.0

## SUMMARY

1. A hot 0.1 per cent ammonium acetate solution of pH 4 was found more satisfactory as a wash for aluminum and iron phosphate in small quantities than cold treatment.

2. An attempt to separate iron phosphate from aluminum phosphate by carefully adjusted pH was unsuccessful.

3. When calcium is present in the aliquot taken in quantities larger than 50 mg., it is necessary to reprecipitate iron and aluminum in order to get quantitative recoveries.

4. Iron phosphate as precipitated in this scheme is of theoretical composition and very little is lost in the washing process.

5. Under the conditions specified in the procedure, iron and aluminum may be separated quantitatively from the more common elements in plant ash, and from each other.

It is recommended that further work be done to determine whether the amount of aluminum phosphate obtained in the procedure is of uniform and theoretical composition; and that further work also include determinations as to the reliability of this procedure with larger quantities of iron and aluminum.

## REPORT ON FRUIT ACIDS

By B. G. HARTMANN (U. S. Food and Drug Administration, Washington, D. C.), *Associate Referee*

The work on fruit acids comprised the collaborative study of the malic acid method described previously<sup>1</sup> and the application of the method to the examination of fruits and vegetables.

A sample of a commercial Concord grape juice and a sample of this juice containing a known quantity of added malic acid were submitted to four collaborators. The results obtained are given in the following table.

COLLABORATOR	GRAPE JUICE	GRAPE JUICE PLUS MALIC ACID	
	MALIC ACID	ADDED	FOUND
	<i>per cent</i>	<i>grams</i>	<i>grams</i>
1	0.31-0.31	0.43	0.42-0.43
2	0.31-0.32	0.55	0.56-0.56
3	0.29-0.29	0.75	0.78-0.78
4	0.31-0.31	1.04	1.23-1.26

The results on the first three sets of samples are very gratifying, the duplicates are excellent, and the amounts found are in good agreement with the amounts added. The results on the sample containing 1.04 grams added acid are not satisfactory. It is intended to continue this work next year.

In the course of an investigation for the purpose of obtaining data on the organic acid constituents of fruits and vegetables, F. Hillig of Food Control Laboratory analyzed 25 fruits and 21 vegetables. With few exceptions malic and citric acids were found in all the materials examined; tartaric was found only in the grape. The methods used have been published in *This Journal*. The data will be published in a future issue of *This Journal*.

In addition to this work the citric acid method was applied to the analysis of oysters, cacao, coffee, malt, the germ and bran of the wheat berry, milk and milk bread. Of six varieties of apples examined for citric

<sup>1</sup> *This Journal*, 15, 848 (1932).

acid—Jonathan, McIntosh, Rome Beauty, Delicious, Grimes Golden and Yellow Transparent—only the last mentioned variety was found to contain the acid (22, 21 and 22 mg. per 100 grams of fruit). This is the first instance of the occurrence of citric acid in apples recorded in Food Control Laboratory. No trouble was experienced with the method in the examination of any one of the materials mentioned. This work is important in the interpretation of fruit analysis, and it is recommended that it be continued.

The method for the determination of inactive malic acid, which has been under investigation the past year, has been published.<sup>1</sup> This method was applied to official samples of fruit sirups by J. B. Wilson of Food Control Laboratory with gratifying results. It is recommended that the method be studied collaboratively.

Considerable time was devoted to the study of methods for the determination of lactic acid in fruit products. The isolation of the acid from the large percentage of sugars contained in jams and jellies presents a difficult problem. The work has not progressed far enough to merit recording here; however, it is believed that next year will see its completion.

#### RECOMMENDATIONS<sup>2</sup>

It is recommended—

(1) That the method for the determination of malic acid described in *This Journal* be adopted as tentative.

(2) That the method for the determination of inactive malic acid described in *This Journal* be studied collaboratively.

(3) That study of methods for the determination of lactic acid be continued.

(4) That the work on the determination of the acids in fruits be continued.

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No report was given on the effect of H-ion concentration on extraction of fruits by the associate referee.

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#### REPORT ON MOISTURE IN DRIED FRUIT

By P. A. CLIFFORD (U. S. Food and Drug Administration, Washington, D. C.), *Associate Referee*

At present drying methods for the determination of moisture in dried fruits are relied upon almost solely. The Association's official method specifies a vacuum drying at 70°C. for 12 hours. It is well understood, however, that any method calling for drying at high temperatures is more

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<sup>1</sup> *This Journal*, 16, 281 (1933).

<sup>2</sup> For report of Subcommittee C and action of the Association, see *This Journal*, 17, 55 (1934).

or less unsatisfactory for products containing such a large proportion of invert sugar as do dried fruits; hence any drying method becomes, to an extent, arbitrary. Other methods based upon principles other than drying have been proposed and will be mentioned briefly later in this report.

The work of R. W. Hilts<sup>1</sup> led to the adoption of the present official method. He recommended a 12 hour drying period because after that period weight losses become fairly constant, and he recognized the fact that drying time is an arbitrary factor. He noted also that by far the greatest proportion of moisture, as gaged by loss in weight, is driven off in 6-7 hours.

In the course of a dried fruit survey conducted by the Food Control Laboratory of the Food and Drug Administration over 400 moisture determinations, most of them in duplicate, were made on dried fruits by the official method. Drying was interrupted at the end of 6 hours and the loss in weight determined, after which the dishes were replaced in the oven and dried 6 hours longer. It was soon noted that 6 hours was ample time to reach a point where the loss in weight per hour of subsequent drying remained constant. In fact, knowing the weight of the dish at the end of the 6 hour period, the weight at the end of the 12 hour period could be very closely approximated by subtracting (on the basis of a 10 gram sample) 0.7 gram for prunes, peaches and apricots.

The most unsatisfactory feature of a drying method for dried fruits is the fact that constant weight is never reached. An experiment wherein a sample of prunes was dried for over 100 hours, weighings being made at 6 hour intervals, proved that constant weight was not reached even over this long period. Instead, when percentage moisture was plotted against drying time a smooth curve was obtained which gradually became flatter so that the apparent moisture increase per hour for the 36-100 hour period averaged 0.015 per cent as against 0.05 per cent per hour for the 6-36 hour period.

It was then desired to know the progress of drying during the prescribed 12 hour period. An experiment was arranged whereby twelve duplicate samples of prunes were placed in the oven, and one dish was removed at the end of each hour until the prescribed time had elapsed. Results are given in Table 1.

The results in Table 1 show that by far the greater portion of water is given off in the first 4 hour period and that the loss in weight becomes practically constant over the 6-12 hour period.

Therefore, as drying indicated by loss in weight is certainly not complete in 12 hours, and as the loss-in-weight method is admittedly arbitrary, why could not a 6 hour drying period be just as satisfactory as a 12? A 12 hour drying period has no more theoretical significance than has a 6 hour period, because it is impossible to tell the point where mechani-

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<sup>1</sup> *This Journal*, 6, 40 (1922); 7, 112 (1923).

TABLE 1.—*Rate of drying during 12 hours*

DRYING TIME hours	MOISTURE per cent	DIFFERENCE per cent
1	16.48	
2	21.60	5.12
3	23.00	1.40
4	23.57	.57
5	24.05	.48
6	24.21	.16
7	24.38	.17
8	24.57	.19
9	24.75	.18
10	24.83	.08
11	25.17	.34
12	25.06	— .11

cally held water is completely driven off and where further losses in weight may be ascribed to chemical changes in the composition of the material. This is due to the fact that the two changes probably take place simultaneously, i.e., decomposition begins before drying is complete. An odor of caramel can usually be detected when the oven is opened at the end of the 12 hour drying period, and a water extract of the dried material is always much browner in color than comparable amounts of the original substance. In the experiment described, where the progress of drying was followed through the 12 hour period, one dish being removed at the end of each hour, water extracts of the dried substance showed a distinct progression in the depth of this brown color. This was so striking that the extracts could be arranged in almost the exact order in which the dishes were removed from the oven. There is evidence of chemical change, too, in the amount of reducing sugars (total as invert) in the dried substance

TABLE 2.—*Reducing sugars before and after drying 12 hours in vacuo at 70°*

SAMPLE	BEFORE	AFTER	DIFFERENCE
	per cent	per cent	per cent
1	42.48	41.00	— 1.48
2	41.89	40.80	— 1.09
3	43.44	42.53	— .91

as compared with the original material. The figures in Table 2 give these data on three samples of dried prunes before and after drying for 12 hours. They show that the reducing power of the sugars before and after drying is lowered by a small but easily measurable amount.

This fact, however, does not necessarily mean that loss in weight due to alteration of the sugars is large. The loss in reducing power, as well as the evidence of caramelization noted above, merely indicates that heating



at 70° causes some destructive change in the sugars present. The resultant loss in weight may in fact be so slight at the end of 12 hours' drying as to be difficult to detect. Experiments wherein samples of prunes were dried for two successive 6 hour periods, then soaked up with 3-4 cc. of water and redried, showed that the weight was practically the same at the end of the second drying period as it was at the end of the first. These

TABLE 3.—*Redrying samples of prunes (per cent moisture)*

SAMPLE	ORIGINAL		REDRIED	
	6 HRS.	12 HRS.	6 HRS.	12 HRS.
1	22.60	23.27	22.66	23.33
2	23.10	23.76	23.10	23.78
3	19.41	20.10	19.43	20.12
4	21.96	22.64	21.98	22.64
5	22.16	22.90	22.17	22.93
6	23.82	24.59	23.83	24.58

results are given in Table 3. However, when the sample of prunes that had been dried for 100 hours was soaked and redried it did not come back to its original moisture figure but gave a result at the end of 12 hours that it had given at the end of 60 hours' drying the first time. In this case there was certainly measurable decomposition.

In any event, no way has been found to determine the point at which mechanically held water is completely driven off or the point where decomposition begins to be noticeable. The results obtained upon drying for 12 hours may be closer to the theoretical value than are results obtained by drying for a 6 hour period, but this point cannot be checked. The writer has found that invert sugar solutions give up their water with difficulty even when dried upon fluffy asbestos, and dried fruits sometimes contain over 50 per cent invert sugar, with usually only 2-3 per cent sucrose. In this connection it may be well to note briefly an experiment performed to check the rate of drying of invert sugar solutions. Commercial invert sugar ("Nulomoline") containing about 2 per cent sucrose was used, a solution being prepared whose refractive index at 20° was 1.4162 = 48.8 per cent solids (from unpublished data of refractive indices of invert sugar solutions of L. H. McRoberts). Knowing that pH is an important factor influencing the stability of fructose to heat, the analyst decided to adjust the solutions to a definite pH before drying. In order to make conditions during drying roughly comparable to those prevailing in an actual sample of dried fruit, buffer solutions were made up by using the actual constituents of a prune ash in approximately their correct proportion<sup>1</sup> and malic acid. The technic was as follows:

Approximately 1 gram of a mixture composed of K<sub>2</sub>CO<sub>3</sub>, 31.5 grams; KH<sub>2</sub>PO<sub>4</sub>, 9.5 grams; Na<sub>2</sub>CO<sub>3</sub>, 5.0 grams; NaCl, 1.0 gram; CaCO<sub>3</sub>, 1.5

<sup>1</sup> Gale and Cruess, *Fruit Prod. J.*, 10, No. 10, June, 1931.

grams;  $\text{CaSO}_4$ , .5 gram; and  $\text{MgO}$ , 2.0 grams was added to a 50 cc. flask and a 10 per cent solution of malic acid was added until approximately the desired pH, as indicated by an appropriate indicator (bromocresol-green, bromphenolblue, or thymol blue) was attained. The solutions were then heated on the steam bath to remove  $\text{CO}_2$  after which they were checked for pH with a quinhydrone cell. The solids in each were then determined by drying an aliquot of each solution to constant weight in vacuo at  $70^\circ\text{C}$ .

In the drying experiments an amount of the invert sugar sirup corresponding to about 5 grams of solids was weighed into a dish containing about 2 grams of fluffy asbestos, and 10 cc. of the buffer solutions was added. Most of the water was allowed to evaporate spontaneously at room temperature and then the samples were heated in vacuo at  $70^\circ$  for successive 6 hour periods. The solids due to the "ash-acid" buffer mixtures were subtracted from the weight of the sugars found on drying.

The results are given in Table 4.

TABLE 4.—*Drying invert sugar solutions at various pH values*

SOLIDS AT END OF—	pH OF ORIGINAL SOLUTION						
	2.6	3.0	3.4	3.8	4.2	4.6	5.0
<i>hours</i>							
6	49.7	49.7	49.8	50.3	50.3	49.7	49.8
12	49.1	49.1	49.3	49.7	49.7	49.4	49.4
18	48.8	48.9	48.9	49.5	49.5	49.3	49.3
24	48.6	48.7	48.8	49.4	49.4	49.1	49.2

The results shown in Table 4 indicate several points of interest. The first is that under these conditions a solution of invert sugar cannot be dried to constant weight within 24 hours. Secondly, the higher solids obtained around pH 4.0 would seem to indicate less destruction of invert sugar at this acidity. It is not known how much and in what direction the pH shifts during drying, but the results roughly check those of Jackson and Matthews,<sup>1</sup> who find the stability of levulose in solution greatest at pH 3.5. Further, if the true solids of the sirup is taken as being 48.8 per cent, as given above, this figure is not approached by even 24 hours' drying at the pH where the sugars seem most stable. (This value may be somewhat in error due to impurities in the commercial invert sugar, but it should not be far from the truth.) It would be interesting to repeat this work along the same lines with possibly a smaller sample, and with invert sugar for which a true value for the solids would be known.

Parenthetically, the pH at which this drying experiment indicates invert sugar to be most stable is about that of dried prunes. Four samples tested showed pH values of 3.8, 3.9, 3.9 and 4.0.

<sup>1</sup> *Bur. Standards J. Research*, Nov., 1933, No. 611.

Admitting, then, the difficulty of obtaining a correct value for solids in dried fruits by drying methods, the writer returns to his original question as to why a 6 hour drying period would not be quite as satisfactory as a 12 hour period. There is no reason to believe that the results obtained by the 12 hour drying are the true ones, and the method, therefore, is arbitrary and the results merely relative. Seen in this light, a 6 hour drying period, if practicable, offers a great advantage in the saving

TABLE 5.—*Collaborative moisture determinations (per cent) on dried fruit*

COLLABORATOR	PRUNES		PEACHES		APRICOTS P		APRICOTS W	
	6 HOURS	12 HOURS	6 HOURS	12 HOURS	6 HOURS	12 HOURS	6 HOURS	12 HOURS
A	16.94	17.55	21.05	21.76	22.22	22.94	26.54	27.32
	17.02	17.59	21.15	21.83	22.29	23.03	26.55	27.32
B	17.08	17.66	21.39	21.99	22.81	23.37	27.35	28.00
	17.07	17.72	21.21	21.99	22.64	23.33	27.37	27.88
C	17.46	17.88	21.42	21.96	22.60	23.19	27.54	28.01
D	17.31	17.89	21.33	21.48	22.51	23.45	26.96	27.75
	17.28	17.83	21.33	22.04	22.53	23.48	26.75	27.68
E	17.20	17.75	21.42	22.23	21.98	23.15	26.74	27.52
	17.53	17.91	21.37	22.06	21.75	23.06	26.72	27.59
F	16.92	17.72	20.96	21.74	22.08	22.95	26.81	27.57
	17.00	17.74	21.11	21.94	22.09	22.95	26.86	27.64
G	17.06	17.55	21.32	21.87	22.02	22.82	26.80	27.67
	17.13	17.59	21.12	21.77	22.40	23.19	26.90	27.60
H	16.97	17.61	20.73	21.57	22.23	23.07	26.54	27.40
	17.03	17.71	20.91	21.71	22.22	23.08	26.36	27.31
							26.72	27.53
I	17.49	17.98	21.70	22.20	22.99	23.69	26.61	27.37
	17.47	17.92	21.78		23.03	23.71	26.59	27.23
J* (75°)	17.44	17.66	22.61	22.90	23.49	23.71	27.67	27.92
	17.49	17.65	22.67	22.88	23.51	23.73	27.70	27.92
K* (100°)	19.97	21.04	24.78	25.92	26.83	28.02	31.64	32.72
	20.20	21.11	24.87	25.97	26.79	27.93	31.57	32.61
Max.	17.53	17.98	21.78	22.23	23.03	23.71	27.54	28.01
Min.	16.92	17.55	20.73	21.48	22.02	22.82	26.54	27.23
Av.	17.17	17.74	21.25	21.88	22.38	23.20	26.82	27.58

\* Not done by official method, so eliminated from averages.

of time, shortening moisture determinations from two days to one day. In routine work this saving of time would be very important.

#### COLLABORATIVE RESULTS ON PRUNES, PEACHES AND APRICOTS

Samples of prunes, peaches and two kinds of apricots were prepared and sent out to eleven collaborators. The method of preparation consisted of grinding several pounds of each fruit three times through a food chopper and kneading and mixing the mass thoroughly after each grinding. Portions of each fruit were then sealed in sanitary cans and sent out with directions to run according to the official method, except that heating be interrupted at the end of 6 hours and weighings made. Results are given in Table 5 and the comments of collaborators follow:

*Collaborator D.*—Temperature between 70° and 71°.

*Collaborator I.*—As the determination is purely arbitrary as to length of time consumed or necessary for drying, I approve of a change of from 12 to 6 hours. Time is a factor in all laboratory work and the 12 hour period is longer than a day's work.

*Collaborator J.*—Temperature reported as 75°. Difficulty was experienced in keeping temperature constant. Necessary to interrupt first drying period at the end of 4 hours.

*Collaborator G.*—It is the opinion of this laboratory that the method involving 6 hour drying, in vacuo, for dried fruits is very desirable and probably more indicative of actual excessive moisture than a longer drying period, which possibly removes water of composition or volatilizes compounds which may be calculated as moisture. We have also found that a sample weighing nearer 5 grams than 10 gives better agreeing duplicates and less difference between the 6 and the 12 hour drying period.

*Collaborator E.*—The increase in moisture is more than 1% in the second drying period in the case of P-apricots. Duplicate determinations agree fairly well, however, and the longer drying time does not appear to be worth while.

#### DISCUSSION

The results, in general, show a somewhat smaller spread between maximum and minimum values reported at the end of 12 hours' drying than at the end of 6 hours. The poorer agreement, however, is not such as to indicate insufficient drying in some cases at the end of 6 hours. Checks between duplicates are on the whole as good at the end of 6 hours as at the end of 12 hours.

Differences in moisture content of the samples submitted might cause some of the differences in results, but the fact that the collaborators were quite consistently either above or below the general average on all samples submitted shows that other factors must have played a part. Some of these factors would be variations in oven temperature, overloading of the oven, poor ventilation of the oven, size of sample, and too long exposure to the air in mixing and weighing.

Temperature control is probably the most important factor. An experiment performed to investigate this effect involved three determinations of moisture made on a sample of dried prunes at temperatures of 65, 70

and 75°. An electrically heated, oil-bath vacuum oven, provided with thermostatic control, whereby temperatures  $\pm 0.5^\circ$  of that desired could be obtained, was used. The average of five determinations at 65° was 25.90 per cent. The average of ten determinations at 70° was 26.32, and the average of five at 75° was 26.65 per cent. This would indicate that a difference of  $\pm 1^\circ$  from the prescribed 70° will cause roughly a 0.1 per cent difference from the value obtained at 70°, and also shows the necessity for close temperature control. The temperatures should not be allowed to vary more than  $\pm 1^\circ$  from that prescribed, if comparable results are to be obtained. Electrically controlled vacuum ovens are much to be preferred, but if they are not available for this work the old-style gas-heated oven can be used with satisfaction. The jacket is filled at least one-half full with a methyl-ethyl alcohol mixture in the proportion of roughly two parts methyl to one part 95 per cent ethyl alcohol, and the boiling point is adjusted to 70° C. by the addition of more of the appropriate alcohol to the mixture. Differences in atmospheric pressure will cause the boiling point to change and it must be watched closely. An efficient condenser is imperative. The expedient of attempting to adjust a gas-fired, water-jacketed oven to 70° should not be resorted to as it is practically impossible to obtain the uniform required temperature with this type of oven. Dishes should be placed directly on the metal shelf of the oven and must not be placed one on top of another. The oven should be allowed to come fully to temperature before the samples are placed in it. A temporary drop in both temperature and degree of vacuum will be caused by the placing of moist samples in the oven, and when the oven is filled with such samples it may require at least three hours to regain a temperature of 70°.

The Associate Referee feels justified in omitting the results of Collaborator J and especially those of Collaborator K, because a divergence from the prescribed temperature was reported.

The matter of the incoming current of dry air is also important, and it should be accurately checked. The prescribed rate is two bubbles per second, but it has been the experience of the writer that most analysts underestimate this rate of bubbling.

Spreading the sample thinly and evenly in the dish is prescribed in the method, but while important, this factor does not seem as necessary as might be imagined. Results are given in Table 6 to illustrate this point. These are duplicate results obtained under identical drying conditions except that in one case the sample was spread evenly and in the other it was allowed to remain in a clump in the center of the dish. Results after 6 hours' drying are reported.

The differences are noticeable, but they do not indicate the necessity of too great care in spreading the sample. This might even be objectionable as resulting in excessive moisture losses during the weighing of the sample. The weighing and spreading operations should be expedited as

much as possible. Choosing the approximate weight of the sample and spreading it in the dish should take but a few seconds. It is unnecessary to weigh closer than 1 mg.

Some of these precautions have been stressed by other investigators. They are repeated here for the sake of completeness and emphasis, particularly as some of these factors become of increasing importance if a 6 hour drying time is to be prescribed.

TABLE 6.—*Effect of spreading of sample in drying dish*

SAMPLE	SPREAD	NOT SPREAD	DIFFERENCE
	<i>per cent</i>	<i>per cent</i>	<i>per cent</i>
1	17.46	17.38	— .08
2	22.86	22.63	— .23
3	16.46	16.35	— .11
4	22.22	21.91	— .31
5	17.39	17.05	— .34
6	22.52	22.15	— .37

Size of the sample is closely connected with another factor, that of overloading the oven. If the capacity of the oven is exceeded, low results are bound to occur. The efficiency of an oven depends on temperature control, the vacuum available, size of the drying chamber, design of the shelves, and, very important, ventilation. In working with very moist fruit the size of the sample might be cut down. In the analysis of hundreds of samples of dried fruit the writer obtained no evidence of incomplete drying at the end of six hours. Ten gram samples were used, and in nearly all cases the oven was filled to capacity with 12 dishes. This was a gas-heated, alcohol-bath, 70° oven with a Cenco pump supplying the vacuum as the line vacuum was seldom high enough. Later work was done with an electrically heated, thermostatically controlled oil-bath oven. To determine whether or not the number of samples in the oven made an appreciable difference in the result, 10 samples of about 10 grams each were placed in it at one time and an average result taken; next only two samples were run. The average figure for the ten samples at the end of 6 hours was 26.32 per cent moisture and the average for the two was 26.39 per cent. The position of the dish in the oven had no noticeable effect on the result. Another run was made with 10 samples of about 5 grams each. The average result was 26.20 per cent. These results lead the writer to believe that *with an efficient oven*, size of sample and number of dishes do not have a very important effect. Further, it is believed that a 10 gram sample is more representative as dried fruits are exceedingly difficult to sample.

These results check the work of Hilts, who concluded that size of sample, varying from 5 to 10 grams, is without influence on the result, and who recommended the larger sample as being more representative. He also

concluded that the method of spreading does not have a very important effect.

However, if tests, such as the one indicated here, show incomplete drying at 6 hours, it is best to use a smaller sample or less dishes at a time for the particular oven. Checks within 0.2 per cent should be expected on properly sampled fruit. In this connection results obtained by Collaborator G, using approximately 9 gram and 5 gram samples, are presented.

TABLE 7.—*Effect of size of sample.*

PRODUCT	WEIGHT OF SAMPLE (APPROX.)	6 HOURS	12 HOURS
	grams	per cent	per cent
Prunes	9*	16.41	17.45
Prunes	5†	17.10	17.57
Peaches	9	20.21	21.44
Peaches	5	21.22	21.82
Apricots W	9	25.49	26.92
Apricots W	5	26.85	27.64
Apricots P	9	21.07	22.60
Apricots P	5	22.21	23.01

\* All 9 gram samples average of 3.

† All 5 gram samples average of 2.

The results in Table 7 definitely indicate incomplete drying at the end of 6 hours for the 9 gram samples, as the spread between the 6 and the 12 hour values is too large. They also show that in one case twelve 9 gram samples were dried at one time and this amount of fruit apparently exceeded the oven's capacity. It is repeated, then, that wherever the efficiency of the oven is in question samples smaller than 10 grams should be used.

#### DRIED APPLES

Dried apples are treated separately in this report because the work was done earlier in the year in the course of regulatory activities by the Food and Drug Administration and the work done on check samples of dried apples submitted here as collaborative study was done by the field stations of this Bureau.

Shortly before this study was undertaken, experimental work had showed discrepancies between the official method for moisture in dried apples and the tentative rapid method calling for heating at 100° C. for four hours, the latter method giving higher results, sometimes by as much as 1 per cent.

Accordingly, a sealed pint jar of ground dried apples was sent to each field station with instructions to report results by the two methods and in the case of the official method to give the results at the end of six hours' drying time as before. Sampling was done by grinding a box of dried

apples three times, mixing in a large pan after each grinding, and finally rolling the sample on an oil-cloth. The results obtained are given in Table 8.

The results in Table 8 show definitely that a higher figure for moisture is obtained by the rapid method. Poorer agreement in results is also noted, a spread of from 27.66 per cent to 26.65 per cent being reported. Much closer agreement is obtained by the official method. Here, as before, all values reported are in satisfactory agreement after a 6 hour drying period and it would seem unnecessary to prolong the drying an additional 6 hours. It will be noted that the difference between the 6 and the 12 hour values by the official method is not so great for dried apples as that noted for dried prunes, peaches or apricots. Some difference in the fruit itself, possibly its more fibrous nature, seems to cause dried apples to give up their water much more readily upon drying.

The degree of vacuum, if once within the range prescribed, does not seem to play an important part in the results.

TABLE 8.—*Collaborative moisture determinations on dried apples*

COLLABORATOR	TENTATIVE METHOD 4 HRS. DRYING		6 HRS.			12 HRS.		
	TEMP.	MOISTURE	TEMP	PRESSURE MERCURY	MOISTURE	TEMP	PRESSURE MERCURY	MOISTURE
	° C.	per cent	° C	mm	per cent	° C.	mm	per cent
A (jar 1)	100	27.16	70	14	26.20 26.29 <sup>1</sup>	70	14	26.45 26.52
A (jar 2)	100	26.89	70	14	26.20 26.22	70	14	26.44 26.47
A (jar 3)	100	26.88	70	14	26.38 26.30	70	14	26.63 26.54
A (jar 4)	100	26.82 26.88	70	14	26.10 26.10	70	14	26.37 26.35
A (jar 5)	100	26.85 26.95	70	14	26.04 26.07	70	14	26.29 26.33
B	98.5	26.76 27.00 26.48	70 ± 1	60	26.14 26.19 26.23	71 ± 2	44	26.44 26.47 26.52
C	99	27.23 27.43						
D	98	27.23 27.10 27.21	70 ± 1	6	26.17 26.26 26.25	70 ± 2	6	26.31 26.40 26.39
E	100 <sup>1</sup>	27.04 26.85	70	28	26.29	70	50	26.54
E	99 <sup>2</sup>	27.64 27.26						

<sup>1</sup> Freas electric oven.

<sup>2</sup> Water-jacketed oven.

<sup>3</sup> Cenco oil-jacketed oven.



TABLE 8.—(Continued).

COLLABORATOR	TENTATIVE METHOD 4 HRS. DRYING		6 HRS.			DRYING IN VACUO 12 HRS.		
	TEMP.	MOISTURE	TEMP.	PRESSURE MERCURY	MOISTURE	TEMP.	PRESSURE MERCURY	MOISTURE
	° C.	per cent	° C.	mm.	per cent	° C.	mm.	per cent
F	95.6	26.78	72	42	26.22	70	45	26.42
		26.87			26.29			26.49
G	102	27.16	71	18	26.18	71.5	18	26.41
		27.26			26.22			26.42
H	94	26.38	70 <sup>a</sup>	28	26.01	70	16	26.29
		26.26			26.06			26.32
H			70 <sup>a</sup>	28	26.29	70	16	26.54
					26.38			26.63
I	98.8	27.14	71	68	26.17	70	63	26.39
		27.14			26.17			26.38
J	95	26.64	72	8	26.21	68.5	8	26.42
		26.68			26.16			26.37
					26.20			26.40
K	100	26.65	70	55	26.11	70.3	64	26.39
		26.66			26.16			26.42
L	97.5	26.73	70	41	26.13	70	38	26.36
		26.92			26.16			26.40
		27.02			26.16			26.40
M	99.5	27.33	67-72	23	26.21	67-72	23	26.27
		27.55			26.21			26.31
		27.93			26.26			26.33
N	99.5	27.47	70	58	25.97	70	58	26.26
		27.51			25.95			26.24
		27.23			25.97			26.27
		27.29			26.02			26.22
O	100	26.82	70	44	26.44	70	44	26.64
		26.60			26.49			26.58
P	99.5	27.04	69	72	25.96	71	75	26.22
Q	99.5	26.91	70	31	26.01	70	32	26.17
		26.85			26.07			26.21
		26.93			26.01			26.17
Max.		27.93			26.49			26.64
Min.		26.26			25.95			26.17
Av.		27.01			26.17			26.39

## SAMPLING PROCEDURE

At about the same time the work described was undertaken some experiments were performed on sampling procedure for apples packed in boxes. It was found that a sample taken in the ordinary way was usually too moist due to the inclusion of too large a portion of apples from the interior of the box. This work led to the formulation of a definite sampling

procedure. The method has been published.<sup>1</sup> It is theoretically exact because apples from the interior of the box and apples near the surface are withdrawn in the same proportion as they exist in the entire box. This method was checked by comparing with the figure obtained by grinding and sampling the entire box and also with the figures obtained by sampling in the usual way. In these experiments the boxes were opened and the inspectors were allowed to withdraw their samples in the usual manner. Then the boxes were turned over and a 1/8 sample was cut from an undisturbed corner. Finally the entire remaining contents were ground rapidly and mixed by rolling and quartering on a large oil-cloth. The other samples were allowed to remain exposed to the air during the preparation of the larger sample so as to give equivalent moisture losses. Results are given in Table 9.

TABLE 9.—*Sampling of dried apples*

BOX NO.	ENTIRE CONTENTS	$\frac{1}{8}$ AT CORNER	INSPECTOR NO. 1		INSPECTOR NO. 2
			A	B	
	<i>per cent</i>	<i>per cent</i>	<i>per cent</i>	<i>per cent</i>	<i>per cent</i>
1	26.34	26.52	26.96	25.93	27.18
2	26.68	26.71	25.43	25.83	
3	26.66	26.50	26.75		

It is seen that the sample from 1/8 of the box at the corner gives results very close to the figure obtained by sampling the entire box, while samples withdrawn by guess may be in error by as much as 1 per cent.

The same considerations would apply to other boxed dried fruits. There are no data on this improved method of sampling, however, except one set of figures on a box of dried prunes. Here the moisture figure for the entire box was 22.24 per cent, while two inspectors' samples were 23.48 and 23.13 per cent, showing again the tendency to include too much moist fruit from the interior of the box. Sampling along the lines outlined for boxed dried apples would undoubtedly give figures much closer to the truth than by the old method.

Other reliable methods for moisture in dried fruit based upon principles other than drying, are the old toluene distillation method and electrical resistance method of comparatively recent development. The general experience with the former has been that the method can easily give erroneous results.<sup>2</sup> This was confirmed by a few experiments in this laboratory. Conditions must be carefully controlled if concordant results are to be obtained and hence the method appears to offer no advantages, outside of a saving in time over the official method.

The electrical resistance method,<sup>3</sup> which is coming into use in the in-

<sup>1</sup> *This Journal*, 17, 66 (1934).

<sup>2</sup> Hiltz, *This Journal*, 7, 112 (1923).

<sup>3</sup> *Dried Fruit Record*, Sept., 1933.

dustry as a rapid method for control work, depends upon the variation in electrical resistance of dried fruits due to moisture content. It is of interest only as a rapid approximate method, as each machine must be calibrated against the official drying method and a chart prepared for each fruit.

#### SUMMARY

(1) The limitations of drying methods for moisture in dried fruit and their arbitrary nature are discussed.

(2) Evidences of chemical change in the sugars of dried fruit during the progress of drying are presented, and an experiment indicating the difficulty of drying and stability at various pH values of invert sugar solutions is given.

(3) The advantages of a shorter drying method are pointed out, and collaborative results are presented to show that a 6 hour drying time gives as satisfactory results as does the official 12 hour period.

(4) The necessity of strictly following the official method is emphasized and the following precautions are stressed: (a) temperature control, temperature variations  $\pm 1^\circ$  from the prescribed  $70^\circ$  will cause (roughly) a 0.1 per cent error; (b) ventilation of the oven; and (c) size of samples and effect of overloading.

(5) Collaborative study on dried apples showing the advantages of a 6 hour drying period in the official method is presented.

(6) Discrepancies between the official method and the tentative rapid method for dried apples are noted.

(7) A sampling procedure for boxed dried fruits is outlined.

#### RECOMMENDATIONS<sup>1</sup>

It is recommended—

(1) That the drying time in the official method for moisture in dried fruits be shortened from 12 to 6 hours.

(2) That the tentative rapid method for moisture in dried fruits be dropped, because better results are obtained by the official method, and also because its main advantage, saving of time, would be lost if the official method is shortened to 6 hours.

(3) That the method outlined in this report for the sampling of boxed dried fruits be adopted as official.

The Associate Referee wishes to express his thanks to V. B. Bonney for direction in the work reported.

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No report on canned foods was given by the associate referee.

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<sup>1</sup> For report of Subcommittee C and action of the Association see *This Journal*, 17, 56 (1934).

## REPORT ON SOILS AND LIMING MATERIALS

By W. H. MACINTIRE (University of Tennessee Agricultural Experiment Station, Knoxville, Tenn.), *Referee*

Conditions during the past year made it difficult to obtain collaborative assistance; nevertheless two contributions were obtained. Of these, one by P. L. Hibbard, of the University of California, is an outline of analyses adapted to the soils of the arid and semi-arid region. It is recognized that the analytical problems of alkali soils differ from those found in the analysis of humid soils. The General Referee, therefore, requested Professor Hibbard to formulate the methods that have proved most acceptable to workers in the regions where the alkali soil occurs (see below).

The Referee also requested a brief on a procedure for the chromic acid, or "wet combustion," method for the determination of organic matter in soils. This contribution was made by J. W. White of the Pennsylvania State College (see p. 334). Both of these papers will be presented in brief form to make them available to those interested and to insure more considered action.

It is recommended<sup>1</sup> that the two papers mentioned be made of record in *The Journal* of the Association with a view to their use in the next revision of methods.

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No report was presented by the Associate Referee on Hydrogen-ion Concentration of Alkaline Soils. The following paper was substituted for that report.

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TENTATIVE METHODS FOR ANALYSIS OF SALINE  
AND SALINE-ALKALINE SOILS

(Also applicable to waters for agricultural uses.)

By P. L. HIBBARD<sup>2</sup> (University of California, Berkeley, Calif.), *Associate Referee*

*Alkali Soils.*—The expression "alkali soils" has the sanction of good usage, but it is not sufficiently specific for scientific use. For the present purpose the following *definitions* are suggested:

Soils that contain amounts of relatively easily water-soluble salts in excess of the amounts common to ordinary soils of humid regions are classed as saline soils.

Saline soils may be acid, neutral, or alkaline.

Acid saline soils contain an excess of hydrogen ion over hydroxyl ion. In alkaline soils, this condition is reversed. In alkaline soils, the excess of hydroxyl ions may

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<sup>1</sup> For report of Subcommittee A and action of the Association, see *This Journal*, 17, 48 (1934).

<sup>2</sup> Presented by W. H. MacIntire.

arise from the presence of  $\text{NaHCO}_3$ ,  $\text{Na}_2\text{CO}_3$ , or silicate complexes which hydrolyze in the presence of water, thus producing excess of hydroxyl ions. Mild alkalinity may be produced by the presence of  $\text{CaCO}_3$  or  $\text{MgCO}_3$  or both. These salts may be present in a soil that also contains alkaline sodium compounds.

1. *Sampling*.—No precise instructions are offered other than those in Chapter I, *Methods of Analysis*, A.O.A.C., 1930. Obtain samples in such manner that they are properly representative, and make explicit statements as to how obtained, depths represented, and describe any characteristic local conditions in respect to vegetation, surface crust, depth to water table, hardpan, rock, etc. See Chapter I, sec. 1, p. 1.\*

2. *Preparation of samples*.—Air-dry and pulverize as directed in I, 2, p. 1

3. *Moisture*.—Proceed as directed by drying at  $100^\circ\text{C}$ ., I, 3, p. 1.†

4. *Preparation of the water extract*.—Use the air-dried material, but weigh out an amount that will contain 100 grams (or other suitable amount), moisture-free basis.

First, determine saturation capacity as directed by Scofield,<sup>1</sup> as follows:

Weigh 100 g. of the dry soil into a soil can having a tight cover, add distilled water, and stir the mixture with a spatula until a condition of saturation is reached. (In its saturated condition, the soil mass should be plastic enough to flow slightly when the container is tipped. The surface should glisten as it reflects light, and all the air should be displaced.) Again weigh the can with its saturated soil and record the increase in weight from the dry condition as "water required to saturate" in terms of percentage of the dry weight of soil. After the amount of water required to saturate the soil is determined, make an extract of an appropriate weight of soil with five times the volume of  $\text{CO}_2$ -free water used in saturating the soil. Place the water in a bottle large enough to hold twice as much, add the soil, stopper the bottle, and shake vigorously till a uniform mixture is produced. Shake again once every 5 minutes for 1 hour. Let stand one-half hour or more to allow coarse particles to settle. Decant the upper portion into a Pasteur-Chamberland filter. Reject the first 50 cc. of filtrate and retain the rest as the soil extract.

*Alternative method*.—Make a 1 to 5 water extract as above described. In reporting results, state which method was used and give actual weight of soil and volume of water used.

#### *Analysis of the Water Extract*

5.  $\text{CO}_2$  and  $\text{HCO}_3$ .—Titrate with standard  $\text{H}_2\text{SO}_4$ , 0.05 or 0.02 *N*, using phenolphthalein and methyl orange indicator, as directed, 54, p. 412. (For colored solution, bromphenol blue or Congo red may be preferable to methyl orange.)

6. *Cl*.—Follow Mohr's method, titrating the neutralized solution from 5 with  $\text{AgNO}_3$ , using  $\text{K}_2\text{CrO}_4$  as indicator, 21, p. 406. (Use of yellow light is advantageous because it gives a sharper end point.)

7.  $\text{SO}_4$ .—Precipitate with  $\text{BaCl}_2$  as in 63, p. 415, or 123, p. 428.

8.  $\text{NO}_3$ .—For solutions low in *Cl*, use the phenol-disulfonic acid method, 17, p. 405. For solutions high in *Cl*, use the *Al* reduction method, 19, p. 406, or the Devarda method, II, 35, p. 23.

9.  $\text{PO}_4$ .—Use the alkalimetric titration method for  $(\text{NH}_4)_3\text{PO}_4 \cdot 12\text{MoO}_3 \cdot 3\text{H}_2\text{O}$ , 70, p. 418 (alternative colorimetric method<sup>2</sup>).

10. *Ca*, *gravimetric*.—Precipitate as oxalate, ignite, and weigh as  $\text{CaO}$ , 60, p. 414, or titrate with permanganate after double precipitation, 20, 21, p. 268.

11. *Mg*, *gravimetric*.—Precipitate as  $\text{MgNH}_4\text{PO}_4$ , ignite, and weigh as  $\text{Mg}_3\text{P}_2\text{O}_7$ , 62, p. 415. (If the solution contains iron, it is advantageous to add about 2% of the volume of citric acid before adding the phosphate.)

\* These references are to *Methods of Analysis*, A.O.A.C., 1930.

† See Appendix, Notes, and Comments.

<sup>1</sup> U. S. Dept. Agr. Circ. 232, p. 9 (1932).

<sup>2</sup> Truog and Meyer, *Ind. Eng. Chem. Anal. Ed.*, 1, 136 (1929).

*Alternative volumetric method for Mg.*—Precipitate as directed above. After the precipitate has been washed free of other salts by the use of dilute ammonia, as usual, remove the ammonia by washing with neutral alcohol several times. Dissolve the precipitate in excess of standard 0.02 *N* acid,  $\text{H}_2\text{SO}_4$ ,  $\text{HCl}$ , or  $\text{HNO}_3$ , using methyl red as indicator. (Solvent action may be hastened by warming on the steam bath.) When the precipitate is *completely* dissolved and the solution remains red, titrate the excess acid with standard 0.02 *N*  $\text{NaOH}$  to yellow end point. One cc. of 0.02 acid = 0.243 mg. of  $\text{Mg}$ .

12. *Na.*—The filtrate from the  $\text{SO}_4$  determination, par. 7, is appropriate. Follow the usual method of removal of  $\text{Mg}$ , etc., by  $\text{Ba}(\text{OH})_2$  and weighing as  $\text{NaCl}$  and  $\text{KCl}$ . Determine  $\text{K}$  as  $\text{K}_2\text{PtCl}_6$ , and compute  $\text{Na}$  by difference, 64 and 65, pp. 415. 416.

*Alternative, Zinc Uranyl Acetate Method*  
(Modification of Kollhoff's<sup>1</sup> procedure by Sokoloff<sup>2</sup>)

REAGENTS

(a) *Uranyl zinc acetate.*—Uranyl acetate ( $2\text{H}_2\text{O}$ ), 300 grams; zinc acetate, 900 grams; acetic acid, 30%, 270 cc.; and distilled water, 2430 cc. Weigh out the salts into a large flask; add acetic acid and water; allow to stand until the salts are dissolved; and filter before use. (Note: Most reagents marked "sodium-free" contain sodium, sometimes in large quantities.)

(b) *Ethyl alcohol 95%.*—Saturated with sodium uranyl zinc acetate. Filter before using.

DETERMINATION

Evaporate to dryness in a Pyrex beaker an aliquot of the solution containing not over 5 mg. of  $\text{Na}$ ; add 10 or 15 cc. of the filtered reagent; stir; and allow to stand for 1 hour or more. Filter through a porous porcelain or glass gooch filter, taking care to transfer all the triple salt into the filter by means of a rubber-tipped stirring rod and some of the reagent. Wash three times with 10 cc. portions of the filtered reagent and pass the washings through the same filter. (Have the filter and the precipitate free from the reagent before washing with alcohol.) Wash twice with 10 cc. portions of the alcohol and, after removing all the alcohol by suction, wash with ether. (It is not necessary to filter the ether, only decant it carefully before use.) Continue suction until the precipitate is dry on the filter.

Allow the crucible to stand in a desiccator for 2 hours before weighing. Dissolve the triple salt in distilled water. Wash the crucible with water until it is free from all water-soluble material, dry in the oven, cool in a desiccator, and weigh. The loss is the weight of the triple salt. (Any possible errors due to phosphate or insoluble matter are thus eliminated.)

$\text{Mg. of } (\text{UO}_2)_2 \cdot \text{ZnNa}(\text{CH}_3\text{COO})_6 \cdot 6\text{H}_2\text{O} \times 1.495 = \text{mg. of sodium.}$

$\times 0.00065 = \text{milliequivalents of sodium.}$

For some purposes, a sufficiently approximate estimation of  $\text{Na}$  may be made by the following calculation:

$\text{M.E. } (\text{CO}_3 + \text{HCO}_3 + \text{SO}_4 + \text{Cl}) - \text{M.E. } (\text{Ca} + \text{Mg}) = \text{M.E. Alkali Bases.}$

13. *K.*—Proceed as in No. 12.

*Alternative Cobaltinitrite Method*  
(Modification of the Kramer and Tisdall Method<sup>3</sup> by Hibbard<sup>4</sup>)

<sup>1</sup> *J. Am. Chem. Soc.*, 50, 1625 (1928).

<sup>2</sup> Private communication, Feb. 2, 1933.

<sup>3</sup> *J. Biol. Chem.*, 46, 339 (1921).

<sup>4</sup> *Methods of Chemical Analysis* (mimeographed). Plant Nutrition, Univ. Calif., p. 9. Rev. July, 1932

## REAGENTS

A: {	113 g. Co(Ac) <sub>2</sub> , 4H <sub>2</sub> O	B: {	220 g. NaNO <sub>2</sub> ,
	300 cc. water		400 cc. Water,
	100 cc. HAc, glac.		

Heat the water to dissolve the salt; when all dissolved, mix equal parts of A and B for use. Force air through the mixture for approximately an hour to remove the red fumes. Preserve from light and ammonia fumes. If not quite clear, filter before using. (As mixed reagent decomposes slowly, mix at one time only enough to last for a few weeks.)

## PREPARATION OF SOLUTION

Evaporate to dryness an aliquot of solution containing about  $\frac{1}{2}$ –2 mg. of K. Dehydrate silica, if more than 0.5 mg. per aliquot is present, by several evaporations in the presence of acetic acid. Filter, and evaporate the filtrate and washings to dryness. (If ammonium salts or organic matter are present, they must be decomposed by igniting the dry residue cautiously. Large amounts of phosphate that may interfere are removed by lead nitrate.)

Add a few drops of HCl and evaporate the solution to dryness in a 50 cc. beaker. Dissolve the residue in exactly 2 cc. of 2 per cent acetic acid. Add exactly 5 cc. of the cobaltinitrite reagent, and after  $\frac{1}{2}$  hour add 5 cc. of alcohol. Cover and let stand 12 hours or longer. Filter on a weighted sintered porcelain or glass filter crucible and wash free of easily soluble matter with 2 per cent acetic acid (30–40 cc.). Dry in oven at 80° to 100° C. Cool and weigh.

Factor to convert  $K_2NaCo(NO_2)_7 \cdot 7H_2O$  to K = .1405.

14. pH.—(Equipment and procedures described are equally applicable to soils, soil extracts, or waters.)

*pH by the Hydrogen Electrode*

Abbreviated and modified procedure of Committee of the International Society of Soil Science method.<sup>1</sup>

## APPARATUS

*Potentiometer*.—Should give readings in millivolts, or pH direct to 0.01 pH unit.

*Galvanometer*.—Sufficiently sensitive to give reliable indications in solutions of low conductivity or little buffer power.

*Platinum electrode*.—About 4 or 5 mm. square, lightly coated with freshly deposited platinum black. (It is advantageous to surround it with a glass jacket to protect it from mechanical injury.) Use great care to avoid poisoning of the hydrogen electrode by salts of mercury or other heavy metals or by any organic compound. When not in use, the electrode should remain immersed in distilled water.

The glass siphon connection between the calomel half cell and the hydrogen electrode vessel is filled with 3% agar gel saturated with KCl. In use, the end of the agar siphon should extend only a little into the suspension of soil and water in the H electrode vessel in order to minimize contact with the heavier soil particles since these are liable to cause drifting potentials.

*H electrode vessel*.—A sintered glass filter funnel in which the filter plate easily permits passage of the hydrogen with very little pressure. Connect the filter funnel by a short rubber connection to an S-shaped glass tube, through which the H passes to the filter plate, and have the outer end of the S tube higher than the surface of the liquid in the filter funnel so that liquid cannot run back toward the hydrogen supply. In starting turn on the H so that it is bubbling up through the sintered glass filter before the mixture of soil and water is added. The flow of H agitates, and prevents passage of the soil mixture through the filter. This device facilitates rapid saturation.

<sup>1</sup> *Soil Research*, 2, 81, 142 (1930).

tion of the soil suspension with H so that equilibrium is quickly attained. If the current of H is likely to remove  $\text{CO}_2$ , or otherwise change the composition of the soil water mixture, use a closed electrode vessel such as the Bollen<sup>1</sup> or the Clark<sup>2</sup> cell.

The hydrogen used may be supplied from a commercial cylinder or be generated by electrolysis. The commercial compressed gas is usually satisfactory without purification. The operator should determine, however, that the hydrogen, from whatever source, is free from more than traces of  $\text{CO}_2$  or oxygen.

Prepare the soil suspension by shaking together for a few minutes one part of soil with two parts of  $\text{CO}_2$ -free water. After the last shaking, allow to settle half a minute, then pour into the electrode vessel enough of the upper portion of the suspension to cover the electrode. Thus the coarser portions of the soil which may cause variable results are kept out of the electrode vessel.

#### *Indicator Method*

For practical purposes, sufficiently accurate results are obtainable by means of indicators. Into three of the depressions in a spot plate place about 0.5 gram of soil; add to each 1 cc. of  $\text{CO}_2$ -free water and mix water and soil. Add 2-3 drops of the indicators: cresol red, pH 7.2-8.8, to one spot; phenolphthalein, pH 8.4-9.6, to another spot; or thymol blue, pH 8-9.5, may be used instead of phenolphthalein; thymol red, 8.5-11.0, or thymol phthalein, 9.5-11.5, are used for the highest alkalinities. Allow to stand 10-20 minutes and read off the pH from the colors developed by means of comparison with buffer solutions, to which the same indicator has been added, or by use of printed color cards.

15. *Carbonate Carbon*.—Wash a weighed portion of soil on a filter with several portions of 0.2 N NaCl to remove  $\text{NaHCO}_3$  and  $\text{Na}_2\text{CO}_3$  before placing the soil in the apparatus to determine  $\text{CO}_2$ . Determine the  $\text{CO}_2$  as described in 6, p. 3.

#### *Alternative Volumetric Method for Carbonate Carbon*

##### APPARATUS

Connect a 100 cc. gas buret at the bottom with a leveling tube by about 3 feet of rubber tubing and add enough mercury to fill the gas buret to zero while some remains in the leveling tube. Connect the top of the gas buret by a short rubber tube to a short, wide-mouthed bottle of 50-100 cc. capacity with a T-tube inserted in the rubber connecting tube. The outlet of the T-tube is closed by a stopcock. Inside the wide-mouthed bottle place a short, wide test tube to hold the acid for decomposing the carbonate.

##### PROCEDURE

Place in the wide-mouthed bottle 5 cc. of water, then 10 grams, or less if high in  $\text{CaCO}_3$ , of soil. Fill the short wide test tube with 10 cc. of HCl (1+1) and set it in the bottle. Insert the rubber stopper tightly. Open the stopcock on the T-tube and bring the mercury in the buret to zero. Close the stopcock on the T-tube and tip the bottle containing the soil and acid so that the acid mixes with the soil. At the same time, lower the leveling tube so that as the  $\text{CO}_2$  is liberated from the soil the mercury in the tube and in the buret remains at nearly the same level. Shake the bottle with the soil and acid in order to secure complete decomposition of the carbonate. When the reaction is completed (1-2 minutes) adjust the level of mercury in the buret and leveling tube to a common level and read off the volume of  $\text{CO}_2$  liberated.

The weight of  $\text{CaCO}_3$  corresponding to the volume found is best determined from tests with known amounts of pure  $\text{CaCO}_3$  by which the apparatus may be calibrated.

<sup>1</sup> *Ind. Eng. Chem. Anal. Ed.*, 3, 203 (1931).

<sup>2</sup> *Determination of Hydrogen Ions*, 3rd ed. Williams and Wilkins, Baltimore, Md (1932).



If 10 grains of soil is taken, 1 cc. of gas equals approximately 0.045% of  $\text{CaCO}_3$  in the soil.

The whole operation requires less than 5 minutes, and no standard solutions are required.

16. *Specific Conductance*.—For the best and most recent description of this determination, the apparatus and results, see Scofield's<sup>1</sup> circular. Report also saturation percentage as determined in No. 3. The apparatus and procedure are applicable to saturated soils and soil extracts, or to waters.

17. *Determination of Replaceable Bases in Soils by Ammonium Acetate Method*.<sup>1,2</sup> —(Suitable for determination of replaceable bases in ordinary non-calcareous, non-saline soils, but if applied to saline or calcareous soils, the results are of uncertain value. For such soils, no satisfactory method for determining replaceable Ca and Mg, as distinguished from water-soluble, is known.)

#### REAGENT

*Neutral Normal Ammonium Acetate*.—Into a suitable bottle introduce about a liter of water, and add 156 cc. of strong ammonia (sp. gr. 0.90) and 119 cc. of glacial acetic acid. Adjust the solution to pH 7 by adding a little more ammonia or acid as necessary, using bromthymol blue as indicator, and dilute to 2 liters. This solution may not be exactly normal in strength, but that is not important for the present purpose.

#### REPLACEMENT PROCEDURE

Pass air-dried soil through a 1-mm. sieve; pass moist soil through a 10-mesh sieve, or otherwise mix as thoroughly as possible. Use 50 grams of air-dried soil, or other suitable quantities. Into a 250 cc. wide-mouthed conical flask, place 80–100 cc. of  $N \text{ NH}_4\text{Ac}$  solution, add the soil, and shake at once. Close the flask loosely with a rubber stopper and set in a water bath at 60–70° C. for 2 hours, shaking once every 20 minutes. Prepare a Büchner filter with a 7 cm. No. 30 Whatman filter, and at the end of 2 hours' digestion, pour the mixture onto the filter, using suction. (If the soil is very fine so that filtration is slow, it may be preferable to use a 9 cm. filter.) Transfer all the soil from the flask to the filter by means of more of the  $\text{NH}_4\text{Ac}$  conveniently supplied from a wash bottle. (The filtrate may now amount to about 150 cc.) Detach the suction, cover the soil with the  $\text{NH}_4\text{Ac}$ , place a cover-glass over it, and allow it to percolate by gravity for about 24 hours, when the filtrate should amount to about 500 cc. (If percolation is very slow, it may be necessary to use some suction occasionally.)

If the soil contains more than 0.5% of  $\text{CaCO}_3$ , stop the extraction when 500 cc. of filtrate is attained. If there is very little  $\text{CaCO}_3$ , continue the percolation with  $\text{NH}_4\text{Ac}$  until the percolate contains almost no calcium, as indicated by a test with  $(\text{NH}_4)_2\text{O}_x$ . It is assumed that when all the replaceable Ca has been extracted, all the other replaceable bases will have been extracted along with the Ca.

Make the filtrate up to a convenient volume, such as 500 or 600 cc., and mix well. Take suitable aliquots for determination of the Ca, Mg, Na and K replaced by  $\text{NH}_4$ .

#### REMOVAL OF AMMONIA AND ORGANIC MATTER FROM THE EXTRACT

Place the appropriate volume of extract in a 200 cc. porcelain casserole and evaporate on the steam bath. When the last of the liquid becomes sirupy, add a little water and shake a little to dissolve the surface film. When nearly dry, add 10–20 cc. of aqua regia (1 part  $\text{HCl}$ , 3 parts  $\text{HNO}_3$ , and 4 parts water); cover with a watch-glass, and heat on the steam bath several hours, or overnight. (The longer

<sup>1</sup> *Loc. cit.*

<sup>2</sup> Schollenberger, *Science*, 65, 552, No. 1692 (1927).

the residue is digested with aqua regia, the easier it will be to burn off the last of the organic matter.) Rinse the cover-glass into the casserole, evaporate nearly dry, and heat on the hot plate very gently to avoid spattering. Ignite below red heat to avoid loss of K or Na until organic matter and ammonium salts are removed. (For this ignition, a low-form multiple jet gas burner is appropriate, or a muffle furnace may be used.) (By this procedure formation of much  $\text{CaSO}_4$  is avoided, so that it does not interfere later in the determination of Na or K.)

If preferred, sulfate the residue in order to avoid possible loss of K during ignition and add to the casserole, before final drying on the steam bath, 1 cc. of  $\text{H}_2\text{SO}_4$  (1+1). Evaporate to dryness and ignite as usual (the residue may be heated to redness without loss of K or Na).

#### DISSOLVING THE RESIDUE AFTER THE IGNITION

Extract sodium and potassium with boiling water, using 5-10 cc. to wash down the whole inside of the casserole. Pass the solution through a 7 cm. Whatman No. 1 filter. Wash the casserole with several 5 cc. portions of water, and pour the solution into the filter. (In this manner all the Na and K will be extracted from the residue by the time 40-50 cc. of filtrate is collected.) Determine Na and K in the solution by methods described previously.

If Ca and Mg are to be determined, add to the ignited residue in the casserole 10-15 cc. of 2 N HCl, cover, boil a few minutes, and transfer to a suitable flask or beaker. Filter if necessary. From the total bases thus found, subtract the water-soluble bases as found in the water extract; the remainder is considered exchangeable.

#### 18. *Exchange Capacity.*—

##### *"Ammonium Absorbed" by Soils, a Measure of Exchange Capacity*<sup>1</sup>

Digest 10-25 gram portion of soil with neutral normal  $\text{NH}_4\text{Ac}$  (50 cc. for each 25 grams of soil) at 60°-70° C. for 2 hours, and transfer to a paper-pulp filter pad, formed on a Witt plate, using gentle suction, and leaching with  $\text{NH}_4\text{Ac}$  until the leachings give no test for Ca. Add 10 cc. of neutral normal  $\text{NH}_4\text{Cl}$  and leach through the soil. Wash out excess  $\text{NH}_4\text{Ac}$  and  $\text{NH}_4\text{Cl}$  with 80% alcohol (carefully adjusted to pH 7.0, using  $\text{NH}_4\text{OH}$  to neutralize any acidity in the alcohol), and continue until only the faintest trace of turbidity develops on the addition of  $\text{AgNO}_3$ . Transfer the soil and paper pulp pad to an 800 cc. Kjeldahl flask with 400-500 cc of water. Add 3-4 grams of  $\text{MgO}$ , and distil into a known volume of standard acid. (Usually 50 cc. of 0.1 N HCl is sufficient.) Test a sample of the original soil for ammonium by the same method and subtract the value obtained from that yielded by the ammonium-saturated soil to determine the ammonium absorbed by the soil. (This is essentially the procedure outlined by Chapman and Kelley, but slightly modified by J. C. Martin.)

#### FORM FOR REPORTING RESULTS OF ANALYSIS OF SALINE SOIL

Sample marked. . . . . Date of Sampling. . . . .  
 From. . . . . Date of Report. . . . .  
 Section. . . . . Township. . . . . Range. . . . .  
 Depth. . . . .  
*Kind of Soil, Class and Name:* Sand, loam, clay, hardpan, etc.  
*pH:* . . . . .  
*Specific conductance.* . . . . .  
*Carbonate carbon:* . . . . .  
*Saturation capacity, percentage:* . . . . .

<sup>1</sup> Chapman and Kelley, *Soil Sci.*, 30, 391 (1930).

*Composition of 5 saturation capacity, or 1-5 water extract, calculated to p.p.m. or milliequivalents in the solution:*

Ca	<i>Note:</i> In most cases, it is not important to determine all of these ions. Usually an approximation of the amounts of Ca, CO <sub>2</sub> , HCO <sub>3</sub> , SO <sub>4</sub> and Cl is sufficient. If desired, the Na may be directly determined by the uranyl-zinc acetate method, or it may be calculated by use of reaction values after all the other principal ions have been determined.
Mg	
Na*	
K	
CO <sub>2</sub>	
HCO <sub>3</sub>	
SO <sub>4</sub>	
Cl	
NO <sub>3</sub>	
PO <sub>4</sub>	
Total dissolved solids	

\* With saline soils or waters it is usually useful to report percentage of Na of the total water-soluble bases, thus  $\frac{(Na+K) \times 100}{Ca+Mg+Na+K}$ , all expressed as mg. equivalents.

## APPENDIX, NOTES AND COMMENTS

(Referring to sections as numbered.)

3. Some prefer to dry at 105° instead of 100° C.

9. For waters or soil extracts, the molybdenum blue colorimetric method for phosphate is adequate and probably preferable in most cases. Perhaps it would be better to place it first, then the alkalimetric titration as alternative.

10, 11, 12, 13. The official gravimetric methods are placed first, though in most cases the alternative volumetric methods are just as reliable, much faster, and do not require so much material.

12. Many analysts do not dry the precipitate of zinc sodium uranyl acetate in the oven, but simply leave it in a dry closed space for an hour before weighing.

13. The gravimetric cobaltinitrite method for potassium has not yet become standardized, so that the analyst should frequently check his procedure by tests with known amounts of potassium.

14. It has been suggested that a water extract of the soil instead of a water suspension be used to determine pH. This is likely to give a different, usually somewhat lower pH. Since a plant must always have its roots in contact with the soil, it seems appropriate to determine soil pH in a water suspension.

15. It is assumed that only CaCO<sub>3</sub> and MgCO<sub>3</sub> are considered as sources of carbonate carbon, hence the necessity for first removing sodium carbonate or bicarbonate. The proposed method needs study. Usually one of the rapid volumetric methods will be quite adequate for estimation of carbonate.

16. It seems unnecessary to describe this procedure in full (as well as some of the others cited), but if this subject is included in the official methods, it will be a very simple matter for the editor to indicate what part of the original articles should be copied by the printer.

17. It is questionable whether methods for determination of exchangeable bases in saline soils should be included in official methods, but the method has been called for, therefore it is included. Probably fairly reliable results for Na and K may be obtained, but for Ca and Mg the figures obtained may be very erroneous.

The form for reporting results may be omitted if desired. It is inserted as a guide for those unfamiliar with analysis of saline soils.

The methods described are, in general, considered precise and if properly executed, may be expected to give reliable results. Many of them are

somewhat tedious and time-consuming. For practical purposes shorter and simpler, but less exact methods, are usually employed by most chemists having to deal with many samples of saline soils. Each analyst uses some system of his own. Consultation with several analysts reveals that they think it desirable to have a description of short, simple procedures which may be used for routine work.<sup>1</sup>

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## REPORT ON REACTION VALUE OF ACID SOILS

By M. F. MORGAN (Agricultural Experiment Station,  
New Haven, Conn.), *Associate Referee*

During the past year there has been some correspondence in regard to standardization of methods of *pH* determination by the quinhydrone electrode, with the results obtained by the glass electrode as a basis of comparison. A recommendation is not ready at this time.

A study of probable errors in sampling in replicate *pH* measurements made at monthly intervals on a series of forty-eight 0.0001 acre concrete walled soil plots over a period of seven years, is now in progress, and a statistical study of these results will be submitted at a later date. Seasonal fluctuations in reaction value are accentuated on heavily fertilized soils, in particular where nitrogenous fertilizers have been applied, necessitating special attention to the choice of season when soil samples are to be drawn for proper evaluation of significant *pH* conditions.

A study of the effects of various nitrogenous fertilizers on the *pH*, exchangeable bases and degree of base unsaturation, as related to losses of bases by drainage and crop removal, is nearing completion, and is expected to give a quantitative measurement of the acid or alkaline tendencies of nitrogenous fertilizers under actual field conditions, thus supplementing Pierre's valuable contributions in calculating the theoretical effects of fertilizers upon the soil reaction.

It is recommended<sup>2</sup> that the duties of the Associate Referee on the Reaction Value of Acid Soils be continued for the ensuing year.

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No report on liming materials was given by the associate referee.

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No report on less common metals in soils was given by the associate referee.

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<sup>1</sup> See *Soil Sci.* [25, 351 (1928)], for methods that have been found satisfactory by the Associate Referee.

<sup>2</sup> For report of Subcommittee A and action of the Association, see *This Journal*, 17, 48 (1934)

## REPORT ON FERTILIZERS

By G. S. FRAPS (Agricultural Experiment Station,  
College Station, Texas), *Referee*

The work of the Referee consisted chiefly in making suggestions to some of the associate referees. Among the subjects studied by the associate referees are the use of selenium in the Kjeldahl method for nitrogen, the estimation of free phosphoric acid in superphosphates, and the sources of some errors in the estimation of potash. Their results, with recommendations, will be given in their reports. The associate referees are entitled to commendation for the excellent work they are doing.

It is recommended<sup>1</sup> that the subject of methods for the determination of manganese, magnesium and the equivalent acidity—or basicity—of fertilizers be referred to the Associate Referee on High Analysis Fertilizers for study.

## REPORT ON PHOSPHORIC ACID

## DETERMINATION OF FREE ACID IN SUPERPHOSPHATES

By WILLIAM H. ROSS, *Associate Referee*, and KENNETH C. BEESON  
(Fertilizer Investigations, Bureau of Chemistry and Soils,  
Washington, D. C.)

The phosphoric acid ( $P_2O_5$ ) in fertilizer mixtures occurs in combinations of free phosphoric acid, mono-, di- and tri-basic phosphates and in such complex compounds as undecomposed phosphate rock. The methods that have been adopted by the Association of Official Agricultural Chemists for the analysis of these phosphatic materials were designed with a view to measuring their availability to plants rather than as a means for determining the content of any phosphatic component. Thus water-soluble phosphoric acid includes such compounds as free phosphoric acid, mono-calcium phosphate and the alkali phosphates. Citrate-soluble phosphoric acid includes dicalcium phosphate, hydrated iron and aluminum phosphates and a portion of any tricalcium phosphate that may be present. Citrate-insoluble phosphoric acid includes the remainder of the tricalcium phosphate, anhydrous iron and aluminum phosphates and undecomposed phosphate rock.

Although free phosphoric acid is properly included in the class of water-soluble phosphates so far as its availability is concerned, it differs from the other members of this class in that it is a very hygroscopic material. The presence of any considerable quantity of free phosphoric acid in a superphosphate or superphosphate mixture therefore greatly interferes with its mechanical condition and the uniformity with which it can be dis-

<sup>1</sup> For report of Subcommittee A and action of the Association, see *This Journal*, 17, 48 (1934).

tributed in the field. Free acid in a superphosphate has the further disadvantage that it has a destructive action on bags and other containers in which the superphosphate is stored. A special method for the determination of free acid in superphosphate is therefore desirable, and a recommendation<sup>1</sup> was adopted at the last meeting of the A.O.A.C. that a collaborative study be undertaken of the relative merits of the different methods that have been proposed for this determination.

Sulfuric acid reacts with monocalcium phosphate, the principal component of superphosphate, to form calcium sulfate and free phosphoric acid. The free acid in superphosphate as normally prepared, therefore, consists largely of phosphoric acid with little or no sulfuric acid. Other acids present in relatively small quantities are fluosilicic and hydrofluoric. For many years these free acids were determined collectively in terms of sulfuric or phosphoric acid by simply titrating an aqueous extract of the superphosphate with standard sodium hydroxide to an end reaction with methyl orange or sodium alizarin sulfonate.<sup>2</sup> This method, known as the titration method, is still used in Germany as one of the alternative official methods of the Verein Deutscher Dünger-Fabrikanten.<sup>3</sup>

The methods most generally used at present are based on the principle of separating the free acids from the other components of the sample by extracting with an organic solvent such as alcohol,<sup>3</sup> ether,<sup>4</sup> or acetone,<sup>5</sup> and determining the free acid in the extract.

In the alcohol and ether methods the extract, or an aliquot, is evaporated to dryness and the free acid is determined in the residue by dissolving in water and titrating with standard alkali, methyl orange being used as indicator. If the extracts contain any volatile acids, such as hydrofluoric and fluosilicic, a greater or less proportion of these acids will be lost in the evaporation of the solvents. Numerous tests have shown, however, that the fluorine in the extract before evaporation is too small to have any serious effect on the results.

That the percentage of free fluorine-containing acids in a superphosphate stored in an open container is likely to be small was shown by adding 1.15 per cent of fluosilicic acid to samples of superphosphate and extracting separate samples with alcohol, ether and acetone. The extracts were then neutralized and the fluorine determined<sup>6</sup> by the Willard-Winter method.<sup>7</sup> The fluorine found in the extracts did not exceed 0.4 per cent on the basis of the sample taken and was usually less than 0.2 per cent. The total free acid was found to be equivalent in each test to the sum of the fluosilicic acid added and the free acid already present. This shows

<sup>1</sup> *This Journal*, 16, 213 (1933).

<sup>2</sup> Ostersetzer, *Chem. News*, 91, 215 (1905).

<sup>3</sup> Methoden zur Untersuchung der Kunstdünge mittel, 6th ed. Braunschweig (1925).

<sup>4</sup> Herzfelder, *Analyst*, 28, 372 (1903).

<sup>5</sup> Shuey, *Ind. Eng. Chem.*, 17, 269 (1925).

<sup>6</sup> The writers are indebted to L. F. Rader of this laboratory for these determinations.

<sup>7</sup> *Ind. Eng. Chem. Anal. Ed.*, 5, 7 (1933).

that an equilibrium is quickly established between the fluosilicic acid and the monocalcium phosphate in the sample to precipitate a salt of the fluorine-containing acid with formation of the equivalent quantity of phosphoric acid. The monocalcium phosphate in superphosphate thus reacts to suppress the concentration of the fluosilicic acid in superphosphate but the extent to which it is suppressed is somewhat less than in the case of sulfuric acid.

In the acetone method an aliquot of the extract is diluted with water and titrated, without previous evaporation, in such a way that no loss of volatile acids occurs. This method should therefore give higher results than the alcohol and ether methods if conditions are such that any significant quantity of a volatile acid would be recovered in the extract. It is improbable, however, as already explained, that such conditions will exist in the analysis of superphosphates prepared as in ordinary commercial practice.

The directions given by Shuey<sup>1</sup> for the acetone method direct that the titration be made to an end reaction with methyl red and then with phenolphthalein. It is claimed that the first titration represents the total free acid; that the difference between the total titration and the first represents the free phosphoric acid alone; and that the excess of total acids over the free phosphoric acid alone gives the other free acids. This would hold true for solutions containing an acid such as sulfuric in mixture with phosphoric. Fluosilicic acid, however, behaves in a titration like phosphoric acid in that twice as much alkali is required to give an end reaction with phenolphthalein as with methyl orange. The end point of hydrofluoric acid does not correspond to that indicated by either methyl red or phenolphthalein. The method outlined is therefore not adapted to the determination of these acids in the presence of phosphoric acid.

To make a collaborative study of the relative merits of the different methods that have been proposed for determining the free acid in superphosphate it is necessary to have a standard sample whose free acid content is known independently of any method of analysis. Monocalcium phosphate, the principal phosphatic component of superphosphate, undergoes partial decomposition in contact with water to form free phosphoric acid and dicalcium phosphate. The latter is less soluble than monocalcium phosphate and the crystals obtained on cooling or concentrating an aqueous solution of monocalcium phosphate will therefore contain a mixture of mono- and dicalcium phosphates.

The separation of dicalcium phosphate may be avoided by crystallization of the monocalcium salt from a solution containing an excess of phosphoric acid. If the acidity of the solution exceeds a certain minimum no dicalcium phosphate will be precipitated, but the crystals will then contain an excess of free acid. This procedure is followed in the preparation

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<sup>1</sup> *Loc. cit.*

of the analytical reagent product and the ratio of  $P_2O_5$ :CaO in the product is therefore greater than the theoretical value for pure monocalcium phosphate.

Clark<sup>1</sup> showed that monocalcium phosphate monohydrate may be prepared free from other calcium salts by dissolving 3 mols of CaO in a phosphoric acid solution containing 10 mols of  $P_2O_5$  in 1800 cc. of water, concentrating at 100°C. to a volume of 1000 cc., and then cooling to 50°C. with constant stirring.

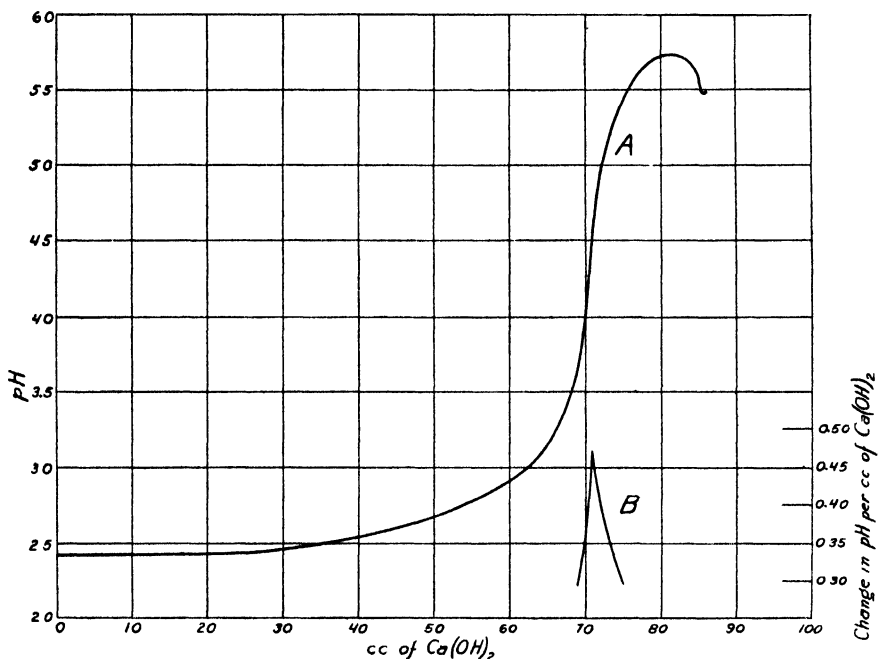


FIG. 1.—A—POTENTIOMETRIC TITRATION OF  $H_3PO_4$  WITH  $Ca(OH)_2$  (QUINHYDRONE ELECTRODE); B—DIFFERENTIAL TITRATION CURVE CALCULATED FROM A.

The salt prepared by this method contained a large excess of free acid. When this was removed by washing in turn with alcohol and ether followed by continuous extraction with ether for 6–8 hours, it was found that the residual material had a  $P_2O_5$ :CaO ratio of 2.541, as compared with the theoretical value of 2.536 for pure monocalcium phosphate. It was also found that the material prepared in this way will dissolve completely when treated with sufficient water to form a M/100 solution and that the solution has a pH value of 4.5.

A solution prepared by adding milk of lime to the equivalent quantity of phosphoric acid of suitable concentration to give a M/100 solution was found to have a pH of 4.35. The free lime used in the test was prepared by ignition of a weighed quantity of calcium carbonate. The stand-

<sup>1</sup> *J. Phys. Chem.*, 35, 1232 (1931).



ard phosphoric acid solution was prepared by direct weighing of chemically pure crystals of the acid<sup>1</sup> that had been allowed to stand over phosphoric anhydride for several years.

The pH value of a M/100 solution of monocalcium phosphate was also determined by a potentiometric titration of phosphoric acid with calcium hydroxide solution. The titration was carried out at 29°C. with a quinhydrone rather than the hydrogen electrode because of the greater ease and speed in obtaining an equilibrium after each addition of the calcium

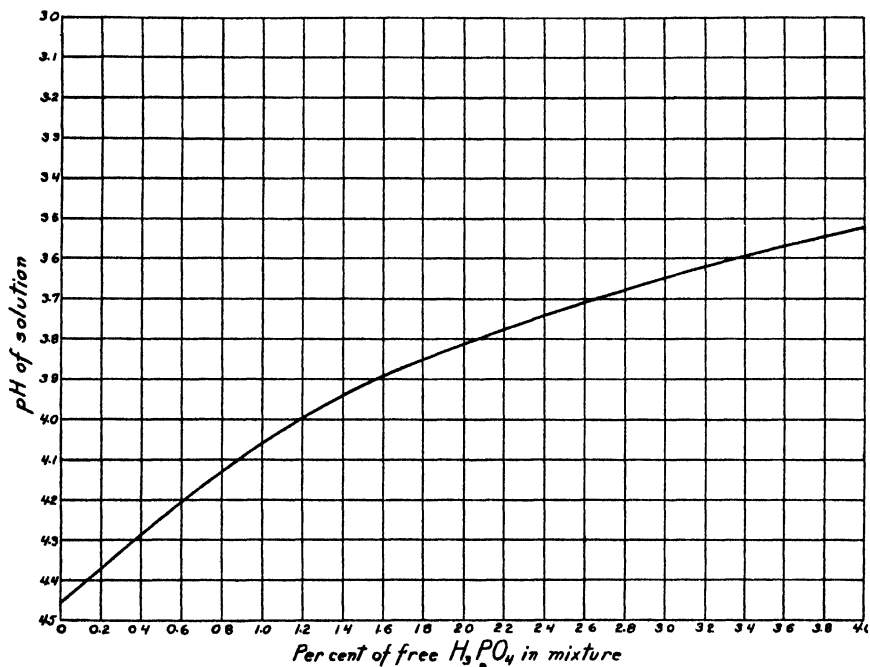


FIG. 2.—pH OF M/100  $P_2O_5$  SOLUTIONS OF MIXTURES OF  $Ca(H_2PO_4)_2 \cdot H_2O$  AND  $H_3PO_4$

hydroxide solution. The concentration of the solution used in the titration represented a M/100 solution of monocalcium phosphate when the end point was reached. The results obtained are shown by the curve in Fig. 1, in which the cubic centimeters of calcium hydroxide solution used in each step of the titration are plotted against the resulting pH of the solution. To facilitate the reading of the end point use was made of the differential titration curve, also shown in Fig. 1. It represents the change in pH of the solution with each successive addition of 1 cc. of the calcium hydroxide solution. The peak of this curve shows that the end point of the titration corresponds to a pH of 4.45.

The mean of the results obtained by these two methods for the pH of a M/100 solution of monocalcium phosphate is 4.40. The pH of a cor-

<sup>1</sup> Ross, Jones and Durgin, *Ind. Eng. Chem.*, 17, 1081 (1925).

responding solution of the salt prepared as already explained by crystallization from an acid solution and extraction with ether is 4.50. It may therefore be concluded that the product obtained by this method of preparation does not contain any free acid. With this information it was possible to prepare a series of standard monocalcium phosphate samples containing known amounts of free phosphoric acid.

The method used in the preparation of these samples involved dissolving a weighed quantity of phosphoric acid crystals in ether, filling to the mark in a graduated flask, adding aliquots of the solution to weighed quantities of neutral monocalcium phosphate, allowing the ether to evaporate, thoroughly mixing the residual material, and allowing it to stand for two weeks.

The *pH* values of the solutions obtained when a sufficient quantity of each sample is dissolved in water to give a M/100  $P_2O_5$  solution are represented by the curve shown in Fig. 2. Having this curve the analyst may readily determine the free acid in an unknown sample of monocalcium phosphate by the simple procedure of making a *pH* measurement of a M/100  $P_2O_5$  solution of the sample. For example, if the *pH* of the solution is found to be 3.7, the free acid present will amount to 2.66 per cent. This procedure thus provides a simple and accurate method for determining free acid in pure monocalcium phosphate or in other phosphates that are known to be completely soluble in the sample taken for analysis. It is not adapted, however, to the determination of free acid in superphosphates owing to the property of some of its more or less insoluble components to undergo partial decomposition in contact with a limited quantity of water.

Table 1 shows the results obtained when solutions of monocalcium phosphate containing known amounts of free acid were analyzed by the so-called titration method. The solutions were prepared by transferring weighed portions of the standard monocalcium phosphate samples to a

TABLE 1.—*Free phosphoric acid in aqueous solutions of monocalcium phosphate by the titration method*

NO. OF SOLUTION	$Ca(H_2PO_4)_2 \cdot H_2O$ TAKEN PER 100 CC. OF SOLUTION	$H_3PO_4$ ADDED	$H_3PO_4$ FOUND
	grams	per cent	per cent
1	1.00	0.50	1.52
2	1.00	1.00	1.59
3	1.50	1.00	2.32
4	1.50	2.00	2.45
5	2.00	0.00	2.87
6	2.00	0.50	2.76
7	2.00	1.00	3.09
8	2.00	2.00	3.39
9	2.00	4.00	4.47

250 cc. flask, filling to the mark, and rotating in a thermostat for one-half hour at 25°C. Aliquots of the solutions were then titrated in the usual way. In Solutions 4 and 9 the acid found showed some approximation to the quantity added. In these solutions the acid present was sufficient to dissolve the greater part of the monocalcium phosphate taken for analysis. In the other solutions a considerable portion of the monocalcium phosphate remained undissolved, and the free acid found was greatly in excess of that originally added. It may therefore be concluded that the titration method cannot be depended upon unless it is known that the volume of the solution is sufficient to dissolve all the monocalcium phosphate in the sample or the quantity of acid present is sufficient to prevent decomposition of the salt into free phosphoric acid and dicalcium phosphate.

The results obtained when the free acid contents of a series of standard samples were determined by the alcohol, acetone, and ether extraction methods are given in Table 2. They show that the values obtained by all three methods are in fairly good agreement with the theoretical and that a variation in the moisture content of the samples up to the maximum of the 10 per cent used in the tests had little or no effect on the results. In the preparation of the samples the water necessary to give the degree of moisture desired was added after the treatment with acid and immediately before the extraction in order to avoid any increase in acidity due to decomposition of the monocalcium phosphate. It was found that the use of 95 per cent alcohol in place of absolute alcohol did not produce any appreciable change in the results.

TABLE 2.—*Free phosphoric acid in monocalcium phosphate by extraction with organic solvents*

FREE MOISTURE IN Ca(H <sub>2</sub> PO <sub>4</sub> ) <sub>2</sub> ·H <sub>2</sub> O.	H <sub>2</sub> PO <sub>4</sub> ADDED	FREE H <sub>2</sub> PO <sub>4</sub> FOUND BY EXTRACTION WITH—		
		ABSOLUTE ALCOHOL	ACETONE	ETHER
<i>per cent</i>	<i>per cent</i>	<i>per cent</i>	<i>per cent</i>	<i>per cent</i>
0.00	0.50	0.40	0.50	0.45
0.00	1.00	1.05	0.95	1.00
0.00	2.10	2.13	2.05	2.05
1.00	2.10	2.06	2.17	2.12
5.00	2.10	2.06	2.07	2.10
10.00	2.10	2.08	2.07	2.05
0.00	4.00	3.90	3.90	3.98
1.00	4.00	3.95	3.92	4.06
5.00	4.00	3.97	3.90	3.91
10.00	4.00	3.94	3.87	4.17

Table 3 shows the results obtained in the determination of free acid in four superphosphate samples. Sample 1 was a fresh superphosphate

only 5 days old at the time of the analysis; Sample 2 was a superphosphate that had been kept in storage for over two years; Sample 3 was a double superphosphate made by treating Florida pebble phosphate rock with phosphoric acid prepared by the sulfuric acid method; and Sample 4 was a double superphosphate made by treating Tennessee phosphate rock with phosphoric acid prepared by the blast furnace method. The values found for the free acid in these samples agree with those in Table 2 in showing that the method of extracting with water, or the so-called titration method, gives higher results than any of the other three methods used in the tests.

TABLE 3.—*Free acid in superphosphate*

NO. OF SAMPLE	MATERIAL	INDICATOR	FREE ACID FOUND BY EXTRACTION WITH—				
			WATER	ALCOHOL		ACETONE	ETHER
				ABSOLUTE	95%		
			<i>per cent</i>	<i>per cent</i>	<i>per cent</i>	<i>per cent</i>	<i>per cent</i>
1	Superphosphate	Methyl Orange	4.83	4.48	4.45	4.02	4.18
		Phenolphthalein	—	4.46	4.50	4.07	4.23
2	Superphosphate	Methyl Orange	2.05	1.62	1.83	1.40	1.66
		Phenolphthalein	—	1.65	1.82	1.37	1.65
3	Double Super-phosphate	Methyl Orange	7.25	5.24	5.26	5.08	5.29
		Phenolphthalein	—	5.30	5.27	5.06	5.09
4	Double Super-phosphate	Methyl Orange	3.77	1.26	1.57	0.90	1.48
		Phenolphthalein	—	1.25	1.67	0.95	1.57

The organic extracts obtained in the analysis of the samples listed in Table 3 showed only traces of sulfuric acid and a maximum of 0.03 per cent of fluorine. It may therefore be concluded that the free acid in these extracts consisted essentially of phosphoric acid. The absence of sulfuric and hydrofluoric acids, but not necessarily of fluosilicic acid, is shown by the close agreement in the results obtained when the titrations were first made with methyl orange, and then to the end point indicated by phenolphthalein.

#### RECOMMENDATIONS<sup>1</sup>

It is recommended—

(1) That a collaborative study be made of the determination of free acid in superphosphates.

(2) That the recommendations relative to the preparation of neutral ammonium citrate solution on which first action was taken at last year's meeting of the Association be adopted (final action).

<sup>1</sup> For report of Subcommittee A and action of the Association, see *This Journal*, 17, 48 (1934).

## REPORT ON NITROGEN\*

By A. L. PRINCE (Agricultural Experiment Station,  
New Brunswick, N. J.), *Associate Referee*

The recent interest in the use of selenium as a catalyst in the determination of total organic nitrogen by the Kjeldahl method necessitates work on its applicability to the determination of total nitrogen in fertilizer materials and mixed fertilizers. Recommendation was made to this effect last year<sup>1</sup> by the Associate Referee, and reference was also made to the work of other investigators along these lines with substances other than fertilizers. A recent paper by L. V. Taylor<sup>2</sup> describes the use of a selenium-mercuric oxide combination in the determination of nitrogen in feed materials. This author found, in general, that the percentage of nitrogen obtained after 30 minutes' digestion in the presence of a mercuric oxide-selenium flux was in agreement with the value obtained after 90 minutes' digestion with mercuric oxide alone. However, when mercuric oxide or selenium was used alone, the nitrogen percentages obtained after 30 minutes' digestion were low.

The Associate Referee decided to try out a comparison of selenium and metallic mercury alone and a combination of these, as well as a copper-selenium combination, on various organic fertilizers and mixed fertilizers. Variations in the length of time for digestion were introduced. The organic fertilizers studied in this connection were fish, tankage, dried blood, two samples of dry cow manure, cottonseed meal, and tung oil cake. The time allowed for digestion with the various catalysts was arbitrarily set at 45, 75, 90, and 120 minutes, respectively; 0.65 gram of metallic mercury was used alone and in combination with the selenium; 0.3 gram of selenium was used alone and in combination with mercury and copper; and 0.2 gram of crystalline copper sulfate served as the source of copper in the copper-selenium combination. The flasks were placed for digestion on an asbestos-covered wire gauze. Gas flames served as the source of heat and were regulated as nearly as possible to the same height. The heat applied was sufficient to keep the liquid boiling at all times, but without distillation of the sulfuric acid.

The results of these determinations are recorded in Table 1. If the digestion for 120 minutes with mercury alone is considered as the standard or correct value, it will be seen at once that digestion for 45 minutes with mercury gave low results in all cases. This might be expected from the appearance of the material at the end of 45 minutes' digestion, when most of the flasks still showed undecomposed organic matter. The results with selenium alone at the end of 45 minutes were quite similar, that is, low

\* Journal Series of the New Jersey Agricultural Experiment Station, Department of Soil Chemistry and Bacteriology.

<sup>1</sup> *This Journal*, 16, 217 (1933).

<sup>2</sup> *Ind. Eng. Chem. Anal. Ed.*, 5, 263 (1933).

percentages as compared with the digestion for 120 minutes, but in most cases the material appeared to be colorless or nearly so. With the mercury-selenium combination the results at the end of 45 minutes check exceptionally well with those obtained for mercury alone at the end of 120 minutes. The copper-selenium combination still showed low percentages of nitrogen at the end of 45 minutes.

With the 75 minute digestion period the mercury and selenium catalyst used alone and the copper-selenium combination showed increases in the amount of nitrogen obtained, but in a number of cases were lower than the standard determination. The 90 minute digestion period was found sufficient to recover all the nitrogen, from all the materials except cottonseed meal, in which case the mercury used alone still gave low results.

It is apparent from these results that when selenium is used alone, the time of digestion cannot be materially shortened over that of mercury without incomplete recovery of nitrogen, even though the digested material appears to be colorless. However, a combination of metallic mercury and selenium, besides materially shortening the digestion period for organic fertilizers, still yields accurate results. However, such a combination necessitates the use of potassium sulfide as a precipitant for the mercury and, in addition to the selenium, increases the expense of the determination.

Several mixed fertilizers and two mushroom soils were next tried out with these catalysts for three different periods, namely, 60, 90, and 120 minutes. As most mixed fertilizers contain nitrate nitrogen, the salicylic acid modification of the Kjeldahl method must be employed for total nitrogen. As salicylic acid contains considerable carbon, the time necessary for complete oxidation to a colorless solution, using mercury alone, was found to be between 75 and 90 minutes. With selenium alone and in combination with mercury or copper this oxidation was found to take place in 40-60 minutes. The first three mixed fertilizers listed in Table 2 were relatively high in mineral nitrogen and low in organic nitrogen. Fertilizer No. 4 had nearly 3 per cent of its nitrogen as organic. The fifth fertilizer had half the nitrogen in the form of nitrate and half in the ammonium form. The mushroom soils were introduced in order to have a material high in organic matter as well as containing some nitrates.

It is apparent (Table 2) that the results with all catalysts are practically as good for the 60 minute digestion as for the 120 minute digestion. This seems a little hard to understand at first, as many of the flasks with mercury alone as the catalyst were still brown at the end of 60 minutes' digestion. However, this coloration was due to the unoxidized carbon from the salicylic acid. Most of the fertilizers tried out contained a relatively small amount of organic matter, which no doubt was easily and quickly oxidized. The organic matter in Sample No. 4 and in the mushrooms soils, although present in considerable abundance, was no

doubt easily oxidized. Nevertheless, the conclusion should not be drawn from these data that the digestion of mixed fertilizers with any of these catalysts may be stopped at the end of 60 minutes, whether the material is colorless or not.

In many cases the organic matter in the mixed fertilizers may be of a resistant character, and to stop the digestion of such material at the end of 60 minutes, with mercury or selenium alone, would mean low nitrogen results. It was also observed in this work that the copper-selenium combination often gave erratic and undependable results, several repetitions being necessary to obtain checks. This combination also required special treatment to prevent excessive bumping in the distillation. It was introduced in the series of determinations with the idea that it might be less expensive than the mercury, especially as no potassium sulfide would be needed prior to distillation.

The only logical conclusion that can be drawn from the data (Table 2) is that selenium used alone has no advantage over mercury as a time saver in the digestion process for determining nitrogen in fertilizers. When used in combination with metallic mercury, the time of digestion may be materially lessened (approximately one-half), but this defeats the purpose of its use by increasing the expense of the operation. If time is the important factor, regardless of expense, the mercury-selenium mixture may be used to advantage. These findings are in accordance with those of previous investigators working on different materials.<sup>1</sup>

During the past year attention has been called to the fact that if cyanamide is analyzed for water-insoluble nitrogen by the A.O.A.C. method for mixed fertilizers (Robertson method),<sup>2</sup> high and variable results are obtained. It should be pointed out that this method was intended for mixed fertilizers and organic substances such as tankage, and not for material such as straight cyanamide. In the official method for such materials, 2 grams of the substance is washed on a filter paper to 200 cc. For determining the water-insoluble nitrogen in cyanamide, the American Cyanamid Company has modified this method as follows: "Grind in a mortar 2 grams of cyanamide in 100 cc. of water. Then transfer to a filter paper and wash with 250 cc. of water." It is probable that the water does not react completely with the cyanamide when it is merely washed with water on the filter. Of course this would be especially true of the granular cyanamide if it were not ground previous to analysis. Furthermore, care should always be taken to allow the water on the filter to run completely through before more wash water is added. The Associate Referee analyzed a sample of granular cyanamide, ground and unground, by both methods. The unground sample determined by the A.O.A.C. method gave variable results ranging from 2 to 4 per cent water-insoluble nitrogen.

<sup>1</sup> Taylor, *loc. cit.*; Osborn and Krasnits, *This Journal*, 16, 110 (1933); Sandstedt, *Cereal Chem.*, 9, 156 (1932).

<sup>2</sup> *Methods of Analysis*, A.O.A.C., 1930, 22.

However, when the sample was ground both methods gave approximately the same results, namely, about 0.5 per cent water-insoluble nitrogen. No doubt it would be safer to grind the sample in water prior to placing on a filter paper, and wash with 250 cc. of water as suggested by the American Cyanamid Company.

# RECOMMENDATIONS<sup>1</sup>

It is recommended—

- (1) That further study comparing the catalysts selenium and mercury

TABLE 1.—*Percentage of total nitrogen in organic fertilizers (different catalysts)*

ORGANIC FERTILIZER	CATALYST	TIME OF DIGESTION PROCESS (MINUTES)			
		45	75	90	120
Fish	Hg	8.03	8.18	8.18	8.20
	Se	8.01	7.98	8.14	8.14
	Hg-Se	8.22	8.20	8.25	8.29
	Cu-Se	8.03	8.16	8.25	8.22
Tankage	Hg	7.27	7.32	7.42	7.31
	Se	7.18	7.21	7.23	7.40
	Hg-Se	7.31	7.36	7.40	7.40
	Cu-Se	7.18	7.36	7.29	7.45
Dried blood	Hg	13.42	13.49	13.51	13.65
	Se	13.40	13.59	13.68	13.57
	Hg-Se	13.66	13.68	13.68	13.76
	Cu-Se	13.38	13.76	13.57	13.72
Cottonseed meal	Hg	6.23	6.23	6.28	6.39
	Se	6.28	6.28	6.32	6.32
	Hg-Se	6.36	6.36	6.36	6.36
	Cu-Se	6.26	6.38	6.32	6.32
Tung oil cake	Hg	5.37	5.43	5.59	5.48
	Se	5.32	5.48	5.54	5.48
	Hg-Se	5.43	5.47	5.45	5.52
	Cu-Se	5.39	5.42	5.54	5.52
Dry cow manure I	Hg	1.71	1.77	1.78	1.77
	Se	1.71	1.69	1.80	1.77
	Hg-Se	1.75	1.80	1.82	1.78
	Cu-Se	1.73	1.80	1.75	1.82
Dry cow manure II	Hg	1.56	1.73	1.73	1.72
	Se	1.62	1.67	1.62	1.67
	Hg-Se	1.75	1.69	1.64	1.67
	Cu-Se	1.71	1.69	1.60	1.69

<sup>1</sup> For report of Subcommittee A and action of the Association, see *This Journal*, 17, 48 (1934).



in the determination of total nitrogen in fertilizer materials and mixed fertilizers be discontinued.

(2) That further study be made of the methods for determining water-insoluble nitrogen in cyanamide.

TABLE 2.—*Percentage of total nitrogen in mixed fertilizers (different catalysts\*)*

MIXED FERTILIZER	CATALYST	TIME OF DIGESTION PROCESS (MINUTES)		
		60	90	120
No. 1, 4-9-7	Hg	3.96	3.87	3.98
	Se	3.89	3.90	3.97
	Hg-Se	3.87	3.83	3.87
	Cu-Se	4.02	3.92	3.82
No. 2, 5-8-7	Hg	4.88	4.85	4.96
	Se	4.90	4.71	4.88
	Hg-Se	4.85	4.92	4.92
	Cu-Se	4.97	4.96	4.96
No. 3, 6-11-10	Hg	5.80	5.73	5.73
	Se	5.73	5.81	5.74
	Hg-Se	5.73	5.81	5.73
	Cu-Se	5.73	5.80	5.75
No. 4, 6-6-5	Hg	6.04	6.07	6.04
	Se	6.04	6.04	6.02
	Hg-Se	6.02	6.04	6.07
	Cu-Se	6.09	6.06	6.17
No. 5, 4.10-7-5	Hg	4.29	4.23	4.29
	Se	4.18	4.23	4.14
	Hg-Se	4.25	4.25	4.24
	Cu-Se	4.27	4.25	4.29
No. 6, Mushroom soil	Hg	2.03	2.08	2.03
	Se	2.06	2.03	2.14
	Hg-Se	2.11	2.14	2.20
	Cu-Se	2.28	2.13	2.14
No. 7, Mushroom soil	Hg	2.03	2.03	2.03
	Se	2.01	2.12	2.03
	Hg-Se	2.01	2.18	2.07
	Cu-Se	2.06	2.28	2.32

\* Analytical work was done by S. J. Toth, Research Assistant in Soil, Rutgers University.

REPORT ON HIGH ANALYSIS FERTILIZERS<sup>1</sup>

By JOHN B. SMITH (Agricultural Experiment Station,  
Kingston, R. I.), *Associate Referee*

Three general problems were considered in planning work for the current year: (1) The suitability of the aliquots prescribed by the various methods when used for high analysis fertilizers; (2) determination of moisture in hygroscopic materials; and (3) comparison of sampling errors with errors in the analytical technic.

## SUITABLE ALIQUOTS

Following a recommendation made by the Referee on Fertilizers, the various methods for fertilizers<sup>2</sup> were examined to see if the aliquots prescribed were suitable for use with mixtures containing greater percentages of fertilizing elements than those for which the methods were originally written. In general, it was found that provision had been made for a proper relationship between the aliquot and the percentage of the element in the material analyzed. Only one change is recommended, that in a rather unimportant instance.

The smallest aliquot permitted for the estimation of water-soluble phosphoric acid by the volumetric method, II, 12, is 0.2 gram. As a large proportion of the phosphates of certain high analysis fertilizers is water-soluble, it seems advisable to make the same provisions for aliquots here as in the method for total phosphoric acid, II, 10, 0.1, 0.2, or 0.4 gram.

## MOISTURE

In 1931 a modification of the Bidwell-Sterling method for the determination of moisture was recommended and adopted as a tentative method.<sup>3</sup> The procedure is simple and the apparatus is available in complete units at relatively low cost. The usual oven-drying process is not permissible for certain fertilizer ingredients that are volatile at 100°C., and the direct process of distillation with toluene seems superior to vacuum drying, but the method should not be recommended as official until collaborative results have been obtained to support it. Samples for collaborative work were prepared, but they were not distributed owing to the absence of the writer from his laboratory. It is hoped that this work may be completed during the coming year.

## SAMPLING AND ANALYTICAL ERRORS

When work on high analysis fertilizers was first undertaken, several requests were made for a study of sampling errors. In response to these requests three shipments of fertilizer were studied. The results for two of

<sup>1</sup> Contribution No. 446 of the Rhode Island Agricultural Experiment Station

<sup>2</sup> *Methods of Analysis, A.O.A.C.*, 1930, Chap. II.

<sup>3</sup> *This Journal*, 15, 46 (1932).

TABLE 1.—Errors of sampling and analysis\*

NITROGEN		TOTAL PHOSPHORIC ACID (P <sub>2</sub> O <sub>5</sub> )		WATER-SOLUBLE POTASH (K <sub>2</sub> O)			
INDIVIDUAL CORES FROM 25 SACKS	COMPOSITE OF 11 CORES	INDIVIDUAL CORES FROM 25 SACKS	COMPOSITE OF 11 CORES	INDIVIDUAL CORES FROM 25 SACKS	COMPOSITE OF 11 CORES		
					1 MM.	0.5 MM.	ALIQUOTS FROM HOMOGE- NEOUS WATER EXTRACT
per cent	per cent	per cent	per cent	per cent	per cent	per cent	per cent
6.93	7.05	13.27	13.68	10.17	10.36	10.36	10.30
7.05	7.03	13.57	13.60	10.40	10.64	10.62	10.36
6.66	7.00	12.80	13.59	9.88	10.54	10.72	10.40
7.07	7.00	13.60	13.66	10.28	10.60	10.34	10.34
7.00	7.02	13.25	13.61	10.38	10.78	10.44	10.36
7.05	7.08	13.77	13.64	9.89	10.26	10.64	10.36
7.04	6.98	13.40	13.59	10.38	10.28	10.30	10.34
6.89	6.97	13.12	13.61	9.59	10.08	10.62	10.40
7.03	7.06	13.42	13.61	10.35	10.48	10.56	10.40
7.03	7.02	13.20	13.60	10.82	10.26	10.42	10.30
7.07	7.10	13.52	13.66	9.42	10.40	10.68	10.32
6.87	7.09	13.47	13.61	9.54	10.20	10.76	10.30
7.17	7.08	13.59	13.64	10.60	10.38	10.70	10.34
7.07	7.06	13.47	13.60	10.12	10.22	10.60	10.30
6.96	7.08	13.50	13.59	10.56	10.44	10.56	10.30
6.97	6.99	13.52	13.60	10.24	10.28	10.70	10.48
7.07	7.03	13.52	13.64	10.47	10.36	10.70	10.20
6.88	7.05	13.55	13.68	10.06	10.42	10.60	10.30
6.76	7.02	13.17	13.60	9.99	10.20		10.34
6.87	7.04	13.42	13.66	10.06	10.48		10.26
6.88		13.87		10.45			
7.07		13.37		10.67			
7.03		13.30		10.64			
7.04		13.17		10.61			
7.33		13.92		10.33			
Mean 6.99 ± 0.02	7.04 ± 0.01	13.43 ± 0.03	13.62 ± 0.005	10.24 ± 0.05	10.38 ± 0.03	10.57 ± 0.02	10.34 ± 0.01
PE <sub>9</sub>	± 0.03		± 0.02		± 0.11	± 0.09	± 0.04

\* Analyses were made by W. L. Adams and A. S. Knowles, Jr. The calculations were made by D. R. Willard

these have been published,<sup>1</sup> and those for the third are included in this report.

The procedure was the same in each instance. A single core was taken from each of 25 sacks from a carload shipment with a sampling tube that could be inserted through the length of the sack. The tube was inserted closed, then opened, and the sample, weighing approximately 120 grams, was withdrawn and transferred to a stopper bottle. The various samples were ground to pass a 1-mm. sieve and analyzed in accordance with official methods. The determinations reported are averages of closely agreeing duplicates. The means and the probable errors of the means were calculated by the usual formulas.

This year, in addition to a repetition of the work reported previously, an attempt was made to find the relative magnitudes of the errors from sampling as compared with those arising strictly from the analytical procedure. Following the analysis of the 25 cores, 11 of the more uniform were selected for compositing to make a single large sample. This was mixed thoroughly, and 20 analytical portions were taken simultaneously for each of the three fertilizer elements and analyzed. The probable errors for single determinations ( $PE_s$ ) were calculated from these results, which represent the magnitude of the analytical error based upon a single determination, in the same way that the probable error of the mean represents the total error, both analytical and that caused by heterogeneity of the original cores. This procedure assumes that complete reliance is placed upon a single determination for each element.

The results are reported in Table 1. It must be remembered that the probable error indicates only that the chances are even that repetition of the work would give values within the limits defined. The probable errors of the means for the 25 cores are quite similar in their relation to the means (Table 2) to those found previously. The relative errors caused by unavoidable variations in analytical technic are shown by the probable errors of single determinations. These are relatively greater than would

TABLE 2.—*Summary of analyses of 25 cores taken from each of three different brands of fertilizer*

	NITROGEN		TOTAL PHOSPHORIC ACID ( $P_2O_5$ )		WATER-SOLUBLE POTASH ( $K_2O$ )	
	MEAN OF 25 CORES	$PE_m \times 100^*$	MEAN OF 25 CORES	$PE_m \times 100^*$	MEAN OF 25 CORES	$PE_m \times 100^*$
		M		M		M
	<i>per cent</i>		<i>per cent</i>		<i>per cent</i>	
8-16-16	$8.14 \pm 0.01$	0.12	$17.30 \pm 0.08$	0.46	$16.17 \pm 0.15$	0.93
8-16-14	$7.81 \pm 0.03$	0.38	$16.84 \pm 0.07$	0.42	$16.68 \pm 0.07$	0.42
7-12-10	$6.99 \pm 0.02$	0.29	$13.43 \pm 0.03$	0.22	$10.24 \pm 0.05$	0.49

\* Expresses the probable error of the mean as percentage of the mean.

<sup>1</sup> *This Journal*, 15, 272 (1932); 16, 220 (1933).

occur in actual practice, for frequently the determinations are made in duplicate and the results are averaged. The determinations for potash exhibit the widest variations, and the greatest analytical error. An attempt was made to reduce this error by regrinding the composite sample to pass a 0.5-mm. sieve in the hope that analytical portions might thus be made more uniform. This resulted in the extraction of a significantly greater quantity of potash but did not greatly improve the uniformity of results. A previous attempt by the writer, using the individual cores of an 8-16-16 fertilizer, also resulted in a significantly greater extraction of potassium compounds.<sup>1</sup> When, however, a homogeneous solution made by mixing together 50 cc. portions from each of the 20 water extracts made for the analysis of the composite sample, was analyzed, the 20 results were much more uniform and the probable error of a single determination was reduced decidedly. This indicates that a considerable part of the analytical error arises in variations in the 2.5 gram portions weighed for analysis, or in the process of extracting these with hot water.

Certain reservations must be made in attempting an interpretation of the results. The number of analyses are too few to be entirely satisfactory. There is no assurance that 25 cores from a single sack might not vary as widely as single cores from 25 sacks. Probable errors set limits between which duplicating results can be expected to fall in only one-half of a large number of replications. These results are based on a single fertilizer.

Obviously, the greatest accuracy cannot exceed the limits of the analytical error. If these results are taken at their face value, it can be calculated that 9, 66, and 5 cores from this material should give probable errors of the mean of the same magnitude as those found for the single determination for nitrogen, total phosphoric acid, and water-soluble potash, respectively.

From another point of view it might be agreed that a variation of  $\pm 0.1$  per cent is a reasonable probable error for the mean in fertilizer work; *i.e.*, that there should be even chances that a resampling of the same 25 sacks would give a value for nitrogen falling between 6.89 and 7.09 per cent. Such a variation is no greater than that apparently caused by the analytical error for potash. Then six cores would be sufficient for potash and these should give a much greater degree of accuracy for nitrogen and potash. Munch and Bidwell<sup>2</sup> have stated that sampling accuracy is proportional to the square root of the total number of units in a lot. Hence, if six cores are sufficient to represent 25 sacks, the square root of any larger number of sacks should be equally satisfactory. The two fertilizers studied previously have shown less uniformity, and would require three times the square root of the number of sacks in a shipment to approximate the accuracy defined above.

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<sup>1</sup> *This Journal*, 15, 272 (1932).

<sup>2</sup> *Ibid.*, 11, 220 (1928).

No definite recommendations can be made until the general subject of accuracy requirements, or of tolerance, is defined by this Association.

#### RECOMMENDATIONS<sup>1</sup>

It is recommended—

(1) That the official methods, *Methods of Analysis, A.O.A.C.*, 1930, 17, 12, line 2, be amended to read, "To an aliquot of the solution corresponding to 0.1, 0.2, or 0.4 g," etc.

(2) That collaborative work be conducted on the present tentative Bidwell-Sterling procedure for moisture in hygroscopic fertilizer salts and mixtures.

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#### REPORT ON POTASH

By L. D. HAIGH (Agricultural Experiment Station,  
Columbia, Mo.), *Associate Referee*

Last year<sup>2</sup> some of the causes for the variation in the potash results by the official Lindo-Gladding method were discussed, and results of trials of suggestions then made were given. It was also suggested that these variations are more likely caused by losses occurring from the final alcohol washings than by other steps of the procedure. The controversy in the past,<sup>3</sup> over strength of the alcohol used, was finally settled by the Association when the use of 80 per cent alcohol was specified in the official procedure.

Moore and Caldwell<sup>4</sup> pointed out that lower results for potash are obtained when 80 per cent alcohol is used than when 92–95 per cent alcohol is used for washing. However, if the stronger alcohol is used for the first part of the washing and 80 per cent alcohol used later, the results will be comparable with those obtained by using strong alcohol alone. This indicates that most of the loss with the 80 per cent alcohol occurs at the beginning of the washing operation.

The solubility of the precipitate of potassium chloroplatinate in alcohol of 80 per cent and 95 per cent strengths was tested by the evaporation of the alcohol after saturation with the precipitate. For 80 per cent alcohol the residue amounted to 7–10 mg. per 100 cc. and for 95 per cent alcohol, to from 0 to 5 mg. per 100 cc. In correspondence with the writer, C. A. Hoag, Chemist of Pomona, California, states that he overcomes this tendency of the 80 per cent alcohol to dissolve the precipitate by saturating the alcohol with potassium chloroplatinate before use.

To test out this modification in the alcohol washing two mixed fertilizers were run for potash according to the official procedure. In one set of

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<sup>1</sup> For report of Subcommittee A and action of the Association, see *This Journal*, 17, 49 (1934).

<sup>2</sup> *This Journal*, 16, 223 (1933).

<sup>3</sup> *Ibid.*, 7, 382 (1924).

<sup>4</sup> *J. Ind. Eng. Chem.*, 12, 1188 (1920).

four determinations 80 per cent alcohol was used according to the official method; in a second set 80 per cent alcohol that had been saturated with potassium chloroplatinate was used. The results obtained are the average of four determinations.

FERTILIZER	OFFICIAL 80%	80% SATURATED WITH $K_2PtCl_6$
	per cent	per cent
2-12-2	1.91	2.02
4-16-4	4.80	4.91

These figures seem to furnish further proof that low results for potash by the official method must be due in part to the alcohol washing.

In a previous report<sup>1</sup> comparative results by the official method and the Fraps method<sup>2</sup> on the same mixed fertilizer were given. These results did not show good agreement. The Fraps method specifies 95 per cent alcohol diluted with hydrochloric acid so that the strength of alcohol actually used is approximately 85 per cent by volume. In order to study the effect of these two alcohols for washing, two fertilizers, as in the previous trial, were run by both methods with the exception that the chloroplatinate precipitates from the Fraps method and the official method were washed with 80 per cent alcohol as prescribed by the official method. The results given are the average of four determinations

80% ALCOHOL FOR WASHING CHLOROPLATINATE  
PRECIPITATE (OFFICIAL METHOD)

FERTILIZER	OFFICIAL METHOD	FRAPS METHOD
	per cent	per cent
2-12-2	1.75	1.73
4-16-4	4.48	4.51

The experiment was then repeated with 95 per cent alcohol diluted with hydrochloric acid, as prescribed by the Fraps method. The results are the average of four determinations each.

95% ALCOHOL (FRAPS METHOD)

FERTILIZER	OFFICIAL METHOD	FRAPS METHOD
	per cent	per cent
2-12-2	1.78	1.78
4-12-4	4.59	4.59

The difference in results obtained by the official and Fraps methods seems to be due to the difference of alcohol washing in the two methods, rather than to the other steps in the determination.

The effect on the results of the different kinds of alcohol washing was also studied by using pure potassium sulfate: 2.5077 grams of Merck's Blue Label  $K_2SO_4$  was dissolved in water and made up to 1 liter, and 10 cc. aliquots were drawn for the potash determinations. The part of

<sup>1</sup> *This Journal*, 15, 277 (1932).

<sup>2</sup> *Ibid.*, 9, 192 (1926).

the procedure requiring ammonium oxalate and sulfuric acid with subsequent ignition was omitted. Four determinations were conducted with each trial. The average result of the four determinations is given.

	ALCOHOL WASHING USED	K <sub>2</sub> SO <sub>4</sub> TAKEN	K <sub>2</sub> SO <sub>4</sub> RECOVERED	
		gram	gram	per cent
Official 80%		.02508	.02452	97.76
80% alcohol saturated with K <sub>2</sub> PtCl <sub>6</sub>		.02508	.0249	99.30
95% alcohol		.02508	.02471	98.53
95% alcohol saturated with K <sub>2</sub> PtCl <sub>6</sub>		.02508	.02483	99.02

To test the effect of ignition on the recovery of the K<sub>2</sub>SO<sub>4</sub>, another series of samples of pure K<sub>2</sub>SO<sub>4</sub> was taken. The aliquots were the same as before. In the first set the potash was determined on the pure K<sub>2</sub>SO<sub>4</sub> salt alone; in the second set, on the pure K<sub>2</sub>SO<sub>4</sub> to which H<sub>2</sub>SO<sub>4</sub> had been added for ignition; and in the third set a solution containing 0.080 gram of ammonium phosphate and 0.010 gram of sodium chloride was added to the pure K<sub>2</sub>SO<sub>4</sub> and evaporated to dryness, H<sub>2</sub>SO<sub>4</sub> was added, and the whole mixture was ignited. The added salts are equivalents of nitrogen, phosphorus and sodium chloride commonly present in a mixed fertilizer carrying this amount of potash. All the samples were washed with 80 per cent alcohol saturated with K<sub>2</sub>PtCl<sub>6</sub> so that the results of the three sets are comparable.

SET NO.	K <sub>2</sub> SO <sub>4</sub> ADDED	K <sub>2</sub> SO <sub>4</sub> RECOVERED		MATERIAL USED
	gram	gram	per cent	
I	.02515	.024727	98.32	K <sub>2</sub> SO <sub>4</sub> alone
II	.02500	.02449	97.96	K <sub>2</sub> SO <sub>4</sub> ignited with H <sub>2</sub> SO <sub>4</sub>
III	.02500	.024513	98.05	K <sub>2</sub> SO <sub>4</sub> ignited with H <sub>2</sub> SO <sub>4</sub> in presence of salts

Apparently ignition may contribute to low results for potash in some cases.

Variations in the potash results may also be due to difficulties in obtaining a constant tare weight of the Gooch crucible. Platinum is deposited on and through the asbestos pad from the alcoholic platinum solution which is poured through it. When the chloroplatinate precipitate is washed from the crucible with hot water, some of this precipitated platinum is washed out of the asbestos, especially if too strong suction is used or the pad is thin or loose enough to allow a rapid flow of water through it with slight suction. To test this point 24 Gooch crucibles were prepared with acid-washed asbestos pads and then washed with hot water, dried, and weighed. The hot water washing was repeated twice, which was sufficient to bring the crucibles to constant weight.

Chloroplatinic acid dissolved in 80 per cent alcohol was poured through the crucibles as in the regular determinations, after which the asbestos pad was washed thoroughly with 80 per cent alcohol, dried, and weighed. The ammonium chloride washing was omitted. The gain in weight of the



crucibles varied from 0.005 to 0.0052 gram, with an average gain for the 24 crucibles of 0.00245 gram. It would have been desirable to repeat the operation until the crucibles ceased to gain in weight, but this was not done.

The loss in weight of the crucible due to the hot water washing was also tested out: 24 crucibles, which had been used for six or eight successive potash determinations, were washed with hot water and slight suction, then dried to constant weight, and the operation was repeated a second and third time. On the first washing the losses in weight varied from 0.0002 to 0.0022 gram, with an average loss of 0.00107 gram; on the second washing they varied from 0 to .0013 gram, with an average value of 0.0005 gram; and on the third washing the average loss of weight was 0.00037 gram. Further trials with the crucibles indicated that pads should be prepared so that under slight suction the water would pass through in drops (3-5 drops per second), not in a solid stream. Such a pad will usually show a constant weight after the second washing with hot water.

The deposition of platinum within the asbestos probably ceases after a few potash determinations have been made, in which case the resulting error would be positive and higher results would follow. If the precipitated platinum is not washed out by the hot water and the tare weight of the crucible is obtained after the hot water washing, this error will be eliminated. A pad should be used to prevent the hot water flowing through in a stream under the ordinary suction. This will minimize or entirely eliminate losses due to any finely divided platinum or asbestos being removed from the pad in the washing operation.

#### RECOMMENDATIONS<sup>1</sup>

It is recommended—

(1) That some collaborative study be made of the losses resulting when the official method for potash is used on pure potassium salts alone and in the presence of the usual accompanying salts.

(2) That comparative studies with the use of 80 per cent alcohol for washing, when saturated with  $K_2PtCl_6$  and as directed by the official method, be conducted.

(3) That in the official method for potash determination, the following paragraph in regard to the preparation of the Gooch crucibles be studied:

Prepare with an acid-washed asbestos pad of such thickness that under slight suction hot water will be drawn through in a series of rapid drops.

(4) That the following suggested change in the last two sentences in par. 43 (a), p. 26, Fertilizers, be studied:

Weigh and remove the chloroplatinate precipitate by washing with hot water,

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<sup>1</sup> For report of Subcommittee A and action of the Association see *This Journal*, 17, 49 (1934).

using slight suction. Wash with 80% alcohol three times, dry as before, and weigh. (Loss equals  $K_2PtCl_6$ .) Calculate to  $K_2O$ .

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The paper, "Determination of Water in Superphosphate," presented by W. L. Hill, will be published later.

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The paper, "Determination of Fluorine in Phosphatic Materials with Special Reference to the Willard and Winter Method," presented by D. S. Reynolds, is published in *This Journal* (see p. 323).

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The paper, "The Equivalent Physiological Acidity or Basicity of American Fertilizers," presented by Mehring and Peterson, was published in *This Journal*, 17, 95 (1934).

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The paper, "The Equivalent Acidity and Basicity of Fertilizers as Determined by the Method Proposed," presented by W. H. Pierre, was published in *This Journal*, 17, 101 (1934).

## SECOND DAY

### TUESDAY—MORNING SESSION

The following address was delivered by H. R. Kraybill at the opening of the Tuesday morning session.

#### SCIENTIFIC PROGRESS AND FEED CONTROL WORK<sup>1</sup>

By H. R. KRAYBILL (Purdue University Agricultural Experiment Station, Lafayette, Ind.)

Increased effectiveness in the enforcement of feed control laws is dependent to a large extent upon advances in our scientific knowledge. Dr. Fraps has stated: "These laws require, to a greater extent than most other laws, a sound basis of scientific investigation and education. Scientific investigation is necessary for the impartial establishment of our definitions, standards and many rulings."

I shall attempt to review briefly the relation of scientific progress to the development of the feed control work and to point out some of the problems that have arisen.

No reliable statistics are available regarding the total tonnage of commercial feeds sold annually in the United States. In several of the states there are reasonably accurate estimates of tonnage based on the sale of state tags or tonnage reports of manufacturers, as required by the state control laws. An idea of the recent growth and current importance of the industry may be obtained from the statistics based on sales of tags for the state of Indiana. In 1911 the estimated sales were 179,000 tons, with a retail value of over \$5,000,000, while in 1930 the sales had increased to 512,096 tons, with a retail value of over \$24,000,000. Thus in a period of 20 years the tonnage has increased three-fold.

The commercial feed industry originated about 1880, chiefly as an institution for the utilization of various by-products. Previous to that time large quantities of by-products from the flour mills, starch factories, breweries, distilleries, cotton gins, etc., were burned, thrown on the dump, or cast into the rivers. The farmer grew practically all the feed for his livestock on his own farm. The limited feed business existing then was confined almost entirely to furnishing simple grain mixtures for such animals as were kept by people living in the cities and towns. The discovery in the early eighties of the feeding value of wheat bran and other by-products through scientific research and feeding trials gave impetus to the growth of the feed industry. The period marked by the beginning of scientific methods of feeding farm animals was that from the establishment of the

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<sup>1</sup> Presented at the Annual Meeting of the Association of Official Agricultural Chemists, held at Washington, D. C., November, 1933.

first state agricultural experiment station in Connecticut in 1875, until 1887, by which time similar institutions had been established in 17 states.

Although the first state feed control law was not passed until 1897, the chemists in the experiment stations and the United States Department of Agriculture were interested in the analysis of feeds long before that time. As early as 1886, at the third Annual Convention of the Association of Official Agricultural Chemists, a committee was appointed to study methods of analysis of feeding stuffs, and thereafter for a period of years extensive work was done. The studies made dealt chiefly with the Weende methods of analysis, by means of which the proximate constituents were determined in five groups. This work stimulated interest in the chemical analysis of various by-products and was responsible for the discovery of the feeding value of many of these products.

As long as the commerce in feeds consisted almost entirely of the pure grains there was little opportunity for adulteration or fraudulent practices. However, when the by-products were introduced various forms of adulteration and deception crept into the commercial feed business. This condition, together with the extravagant and fraudulent claims made for various condimental stock foods, resulted in the enactment of state feeding stuff control laws.

The first state law regulating the sale of commercial feeding stuffs, mentioned previously, authorized the Massachusetts Agricultural Experiment Station to sample and analyze for fat and protein all commercial feeding stuffs offered for sale in the state and to publish the results. No provision was made for a guarantee, and no penalty was provided for the adulteration or selling of inferior feeds. Connecticut had passed a food law in 1895, which also included foods for domestic animals, but in the administration of the law only foods for humans were included. In 1897 the state of Maine enacted a more comprehensive feeding stuffs law, which served as a model for laws which were passed by New York, Rhode Island, Vermont and Connecticut. During the next decade many other states enacted similar laws. At present 46 of the 48 states have feed control laws.

In 1906 the Federal government enacted the Food and Drugs Act, which applies to food for domestic animals when placed in interstate commerce.

One of the early problems arising in feed control work was the lack of uniformity of laws, rules and regulations in the various states. On account of this situation a conference was called of the Feed Control Officials from the various states and the Federal government. This resulted in the formation, in 1910, of the Association of Feed Control Officials of the United States. The object of the Association is "to promote uniformity in legislation, definitions, rulings and the enforcement of laws regulating the manufacture, sale and distribution of feeding stuffs."

Increased efficiency in feed control work is dependent very largely upon progress in the development of both the methods of analysis of feeds and of knowledge of the principles of nutrition. Twenty-five years ago it was commonly believed that the essential constituents of a feed were carbohydrates, protein, fat and mineral matter and that a measure of the amounts of these materials present in a feed was sufficient to give a fair estimate of its value. Consequently the chief provision of the feed control laws is a guarantee as to the minimum percentage of fat, protein and carbohydrates and the maximum percentage of crude fiber present. In addition to this a statement of each ingredient contained therein is required. The laws are primarily those for correct labeling, and they are directed towards furnishing the consumer with information which will enable him to evaluate the feed. During this early period of the control laws interest in nutritional studies was centered in the determination of the digestible nutrients, net energy values, the total protein requirements, and to some extent in the mineral requirements of various types of livestock. It was not generally recognized that equal quantities of digestible proteins may have widely different nutritive values and that other accessory food substances discovered later were essential for the nutrition of the animal. Thus the current information on the principles of nutrition determines very largely the type of the control work.

The chemical studies of Osborne and his associates, from 1890 to 1908, in the preparation of pure proteins paved the way for a better understanding of their nutritive value. The studies of the amino acid content of purified proteins of economic importance laid the foundation for the extensive work on their nutritive properties which he carried out in collaboration with Professor Mendel from 1909 to 1928. It was demonstrated that the failure of animals to grow on a diet of which zein, the chief protein of corn, was supplied as the protein source was due to the lack of tryptophane and lysine in the protein. When these amino acids were added to the diet growth was obtained. It was similarly shown that gliadin could be made adequate for growth by the addition of the amino acid lysine, in which it is deficient. This led to many investigations to determine which ones of the twenty or more amino acids known are essential for animal life. Although much work remains to be done it is now generally believed that at least tryptophane, lysine, cystine, and histidine are necessary. Thus it was shown that the amount of digestible protein is not a measure of the feeding value of the protein in a feed. The nutritive value of proteins is at least in part related to the various essential amino acids that they contain.

In 1906 Hopkins showed that normal nutrition requires other substances besides proteins, fats, carbohydrates and minerals. He states: "No animal can live upon a mixture of pure protein, fat and carbohydrates and even when the necessary inorganic material is carefully sup-

plied, the animal still can not flourish. The animal body is adjusted to live either upon plant tissue or other animals and these contain countless substances other than the proteins, carbohydrates and fats."

In 1911 Funk first claimed to have isolated an active substance which was protective against the disease of beriberi in man and polyneuritis in fowls. He named the substance "beriberi vitamine." Then, in 1913, McCollum and Davis and Osborne and Mendel independently and almost simultaneously discovered the existence of a necessary food substance which later was designated as vitamin A. Following this there resulted very extensive studies on vitamins, until now at least six are definitely recognized, and there is evidence of still more.

Advances have also been made in our knowledge of the rôle of mineral elements in the nutrition of farm animals. Attention has been centered chiefly on the importance of calcium, phosphorus, sodium chloride and iodine. The importance of the ratio of calcium to phosphorus is recognized. The need for other elements in smaller quantities, such as iron, copper and manganese, has been demonstrated.

Coincident with the rapid progress in the science of nutrition during the past 25 years much progress has been made in feeding practices. Through breeding and better feeding methods high production strains of animals have been produced. This is especially striking in the case of poultry and dairy cattle. The tendency to produce more poultry under conditions of confinement than under range conditions and to keep large dairy herds of high production capacity in dairies with little or no pasture range makes it necessary to insure rations which are complete in every detail. This condition has increased the production of mixed feeds for special purposes. It is interesting to note from statistics in Indiana that while during the last 20 years there has been very little change in the amount of mill feeds sold, there has been a very large increase in the amount of special purpose feeds, which include the proprietary mixed feeds for cattle and swine and the poultry mashes. This development has emphasized the importance of considering other necessary food factors besides carbohydrates, proteins and fats. It has also increased the importance of the enforcement of the feed laws and brought many new problems before the control officials.

Since the importance of vitamins has become well recognized, various feeding stuffs have been developed especially to furnish vitamins. The use of cod liver oil because of its potency in vitamin D is a common practice. Recently the practical use of certain other fish oils as a source of vitamin D has been demonstrated. Preparations of vitamin D concentrates from fish oils and irradiated products with vitamin D potency are available. These developments have made it necessary for the control chemist to extend his tests to include vitamin potency. Unfortunately no reliable chemical tests are available, and it is necessary to use the more tedious

biological methods. Several of the states are now testing products for their vitamin D potency. In 1930 the Association of Official Agricultural Chemists appointed a referee on this subject, and is now actively engaged in a study of methods for vitamin D testing.

The recent scientific advances bring many new problems to the control chemist, and I wish to present briefly a few of them. Only by understanding more fully the principles of nutrition and developing new chemical and biological methods for testing feeds can we expect to make real progress.

The problems of vitamin testing and regulations regarding labeling are difficult ones. It should be remembered that the state laws provide against "misleading" as well as "false" labeling. To label a product as rich in vitamins or to include the word vitamin in the brand name when the product is rich in only some of the necessary vitamins is certainly misleading. It is on account of the danger of misleading the consumer that the Association of American Feed Control Officials has gone on record as condemning the use of the word vitamin or any contraction of the word vitamin in the brand name of a feeding stuff.

The question as to what concentration constitutes richness in a vitamin is also difficult to answer. The ordinary feeding stuffs contain various amounts of all the vitamins. How much of each vitamin must a product contain before it may be truthfully called rich in vitamins? Professor Sherman in addressing this organization two years ago made the following statement: "Without detailed argument it may be said that a careful thinking-through of this subject is likely to bring each of us sooner or later to the view that—withstanding the difficulty and expense of their determination—numerical expressions of vitamin values will be found both important and inevitable, not only in the case of drugs offered as vitamin concentrates but also ultimately of all foods and feeding stuffs which are offered to the public as good sources of vitamins."

On the other hand there is no evidence that the ordinary feeding stuffs do not contain an abundance of certain of the vitamins of which vitamin E is an example. If this is true, is there any merit in claiming richness for an ingredient in a feeding stuff for which there is no practical value? The whole problem is one which readily lends itself to false and misleading representation unless it is dealt with in a sound manner. As mentioned earlier several states are now testing products for vitamin D activity. A good start has been made, but much more work is needed. It will doubtless be necessary to develop methods for other vitamins as they become of more importance in feeds.

The problem of measuring the quality of proteins is extremely complicated because protein requirements for growth, for maintenance, for milk production or for egg production may vary, and then too in most cases not all the protein of the ration is derived from the commercial feed. We know that the different proteins have supplementing properties so that

the value of the protein in a feed will depend upon what other feeds are fed with it in the ration. We do not know, however, what levels of the essential amino acids are required in a ration, and if we did know we would not have accurate methods for the quantitative determination of these amino acids in feed mixtures. Furthermore we do not yet know whether such information and methods, if available, would enable us to evaluate the proteins satisfactorily. There may be other unknown factors involved.

The requirement of stating each ingredient in a mixed feed has been of some value in a small measure in this connection as there is available considerable information regarding the nutritive value of the proteins of the various ingredients of feeds. But this raises the problem as to how much of each ingredient must be used before it may be listed as an ingredient. Obviously claims should not be made for ingredients unless they are present in sufficient quantity to have the expected nutritive effects. While the presence of these ingredients can be detected quite accurately qualitatively, no suitable methods for their quantitative estimation are available. For a number of years this Association has been studying microscopic methods for the identification of ingredients and also methods for the quantitative determination of ingredients. Some progress has been made in methods for the determination of grit, hoof meal, oat hulls and other ingredients, and there is real need for the development of quantitative methods of estimating the various ingredients in all feeding stuffs.

Animal tankages are used very extensively by swine feeders as a supplement to corn. It has been recognized for some time that the total protein content of these materials is not an accurate index of their nutritive value. In some studies of the hot-water-soluble and hot-water-insoluble fractions of tankages, Curtis, Hauge and Kraybill have shown that neither the soluble fraction nor commercial "stick" has any material value when used as a supplement to the protein of corn alone, due chiefly to a deficiency of tryptophane. Because of their lysine content these soluble fractions may have some value in supplementing a combination of the proteins of corn and wheat bran. This work indicates that a determination of the hot-water-soluble protein in tankages may be of some help in determining their nutritive value. Further studies are necessary to ascertain the value of this determination.

Recently we had a request to accept for registration as a feeding tankage a product that was derived from hide trimmings. It seemed probable that this product would have no more value than "stick" as a supplement to corn. We carried out experiments with albino rats, comparing the tankage as a supplement to corn at a total protein level of 14 per cent (8.0 per cent from corn and 6.0 per cent from the tankage) with a regular digester tankage at the same protein level and with corn alone. The average weekly gain on the regular digester tankage was 12.0 grams, with the tankage from hide trimmings 4.0 grams, and with corn alone 3.4 grams.



These results show that the tankage from hide trimmings was much inferior to the ordinary digester tankage and was of practically no value as a supplement to corn. On the basis of these results the manufacturer was advised to divert the material to fertilizer tankage, and registration of the product as a feeding tankage was refused.

Recent interest in the study of the toxic effect of fluorine emphasizes the need of regulations controlling the amount permitted in mineral feeds. The problem is complicated by reason of the cumulative effects and also because satisfactory methods are not available for determining the fluorine content of feeds. There is need for a thorough study of this problem.

In the present definition for meat scraps, if the product contains bone in excess of the equivalent of 10 per cent of  $P_2O_5$ , it is required that it be labeled meat and bone scraps. Recent studies in poultry nutrition have shown that the trouble known as "slip tendon" may be associated with too much bone in the ration. In order to guard against an excess and at the same time insure sufficient calcium and phosphorus in the ration it is necessary for the feeder to know the approximate  $P_2O_5$  content of the meat scraps or meat and bone scraps. To show just what the situation is at present I have compiled the records of analyses of these products in Indiana for the last three years. One hundred and nine samples of meat scraps showed a maximum of 12.96 per cent, a minimum of 3.42 per cent and an average of 9.12 per cent of  $P_2O_5$ , while 202 samples of meat and bone scraps gave a maximum of 14.56 per cent, a minimum of 7.27 per cent and an average of 10.24 per cent of  $P_2O_5$ . These records indicate the advisability of requiring a more accurate guarantee of the  $P_2O_5$  content of these products.

As mentioned previously, in recent years there has been a marked increase in the sale of so-called "special purpose" feeds of which the "poultry all mash" is an example. Such a feed is intended to furnish a complete ration for the hen without any supplementary feed. If the feed so labeled will not fulfill the requirements indicated by the label it would clearly seem to be misbranded, just as much as if one of the guaranteed ingredients were left out of the feed. How to control these special purpose feeds offers some real problems. Recently several of the states have fixed standards of analysis for special purpose feeds. While such standards are of some value they are not sufficient to insure that the feed will satisfy the intended purpose because the analysis not an accurate index of the nutritive properties of the feed. Perhaps it will be necessary to resort more and more to biological methods as supplements to chemical methods.

In conclusion I might state that I have indicated only a few of the many problems in feed control work. The solution of these problems and increased efficiency in feed control work will depend largely upon scientific progress.

## REPORT ON PLANTS

By O. B. WINTER (Michigan Agricultural Experiment Station,  
E. Lansing, Mich.), *Referee*

Last year it was recommended that methods for making the following determinations on plant materials be studied during the year: (1) Forms of nitrogen, (2) less common elements, (3) chlorine, (4) sodium, (5) carbohydrates, and (6) fluorine. Associate referees were appointed on each of these problems with the exception of fluorine. Methods for the determination of this element have been studied by the Associate Referee on Fluorine and by other associate referees of this Association. The Referee on Plants is studying a colorimetric method.

No formal report will be made on Carbohydrates in Plants. J. T. Sullivan, Associate Referee, made a study of methods for the determination of starch and will continue his work. No formal report will be made on Less Common Elements in Plants. J. S. McHargue, Associate Referee, has done some work on methods for the determination of iodine and fluorine, and is working on a combustion method for the preparation of plant materials for analysis which will include all four of the halogens in one large sample of material.

Lillian Butler, the Associate Referee on Sodium in Plants, has done some work on methods for the determination of potassium, and her report will include this subject. The Referee recommends that the study of methods for the determination of sodium in plants also include a study of the methods for the determination of potassium.

The other methods will be reported by the associates, and the Referee concurs in their recommendations.

It is recommended<sup>1</sup>—

(1) That the associate referees continue their studies of the methods for making the following determinations on plant materials: Forms of nitrogen, less common elements, chlorine, sodium and potassium, and carbohydrates.

(2) That methods for the determination of fluorine in plants be further studied in cooperation with the associate referees in other sections who are interested in the determination of this element.

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No report on less common metals in plants was given by the associate referee.

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<sup>1</sup> For report of Subcommittee A and action of the Association, see *This Journal*, 17, 49 (1934).

## REPORT ON TOTAL CHLORINE IN PLANTS

By HERBERT L. WILKINS<sup>1</sup>

The official method for the determination of chlorine in plants assumes the absence of interfering amounts of fluorine, bromine, or iodine. The work here reported depends on the further assumption that the chlorine in plant material occurs either as chlorides or that it is all readily converted into compounds which react with silver nitrate to form silver chloride. This view is held by Pettinger,<sup>2</sup> Sjollema and Dienski,<sup>3</sup> and possibly others.

According to Sjollema and Dienski all the chlorine is recovered from such materials as grass, corn meal, and soybean meal by extraction with hot water. However, it was felt that this method of separating chlorine from the sample is not likely to be of very general application. No determinations were made by this method.

Considering the work of Thompson and Oakdale<sup>4</sup> and the second of the above assumptions, the writer attempted to separate chlorine from the sample as hydrochloric acid by treating the sample with sulfuric acid and steam distillation. If very concentrated sulfuric acid is used, there is satisfactory separation and recovery of chlorides in a reasonable volume of distillate, but if the acid is diluted with more than half its own volume of water a large quantity of distillate is required to recover all the chlorine. When the stronger acid is used appreciable quantities of other substances are also removed from the sample. Large quantities of sulfur dioxide are given off and a white, sparingly soluble substance is also observed in the distillate even if filter paper is the test material. Very likely this distillate would require further treatment before it would be a suitable medium in which to determine chlorine.

Recently Davies<sup>5</sup> devised a method for use with dairy products and then applied it to a variety of other materials. He heated the sample with approximately 25 per cent nitric acid and a strong solution of potassium permanganate in the presence of an excess of silver nitrate, and after cooling and adding urea and acetone to improve the end point applied the usual Volhard titration. With grass this process did not yield a solution in which the end point could be seen readily. Attempts by the writer to apply the Mohr titration to the neutralized Davies solutions (omitting urea and acetone) failed, either because the resultant concentration of electrolytes was so high that the precipitate did not stay in suspension, or because color developed in neutralization. Preserving the suspension by adding gum Ghatti improved the situation but little. This titration

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<sup>2</sup> *J. Agr. Research*, **44**, 919 (1932).

<sup>3</sup> *Biochem. Z.*, **245**, III, 76 (1932).

<sup>4</sup> *J. Am. Chem. Soc.*, **52**, 1195 (1930).

<sup>5</sup> *Analyst*, **57**, (2), 71 (1932).

can be made with sufficient accuracy in a volume of 300 or 400 cc. if a reference color is used (*e.g.*, add excess chloride to a solution of similar composition to the unknown one and produce a similar quantity of precipitate in it) and due account is taken of the quantity of standard solution required to produce the end point in this volume, provided the precipitate is held in suspension by non-interfering means.

The method of Van Slyke<sup>1</sup> as modified by Christy and Robson,<sup>2</sup> an iodometric one, depends on the formation of iodine by the reaction of potassium iodide with potassium bi-iodate in acidic (and as used by these authors also protein-free) solutions. The reaction is given as  $\text{KH}(\text{IO}_3)_2 + 10\text{KI} + 11\text{HNO}_3 \rightarrow 11\text{KNO}_3 + 12\text{I} + 6\text{H}_2\text{O}$ . Because the end points were indefinite over-titration resulted from attempts to apply this method to the filtrates obtained from the Davies digestion. Treatment of the filtrate with potassium permanganate improves the procedure, but before an end point can be obtained with this reagent a dark colored precipitate forms.

In titrating silver nitrate with potassium iodide by this method more than the equivalent amount of the latter is required unless there is already present in the solution silver iodide equivalent to about 20 mg. of chlorine. After this amount of silver has been titrated in the solution, the subsequent titrations give the expected values, even when gum Ghatti is added to hold the precipitate in suspension (see Table 1).

Because of the unsatisfactory results obtained when attempting to determine the excess of silver nitrate in the filtrate from the Davies digestion, the writer thought that the precipitate would offer a means of estimating the amount of silver nitrate required to precipitate the chlorine in the sample. Some of these precipitates, with the filter papers, were ignited at 600°C. in resistance glass beakers. The resulting ash was treated with concentrated sulfuric acid and heated until white fumes were evolved, diluted with water, and titrated with potassium iodide. As it was difficult to bring all of this ash into solution, it was thought that the organic material as well as the chlorine content of the precipitate could be removed by a Kjeldahl digestion. Preliminary tests showed that the end point color would develop in the strongly acid solution. A few determinations were made on Sample 213 (a KI solution of which 1 cc. is approximately equivalent to 0.001 gram of chlorine being used) with the following titrations resulting: 18.25, 18.50, 18.15, 18.20, 18.30, and 18.13. The range from high to low amounts to approximately 0.37 mg. of chlorine. The end points obtained in these diluted digests were not so good as were obtained in the preliminary tests.

Further modifications in the proportions of several of the reagents used resulted from tests which showed that 0.5 gram of copper sulfate is enough for the Kjeldahl digestion and that one-half as much bi-iodate as is used

<sup>1</sup> *J. Biol. Chem.*, **58**, 523 (1923).

<sup>2</sup> *Biochem. J.*, **22**, 571 (1928).

in the original method and twenty times as much starch give better results than the amounts of these which were used previously. Even in the limited use which has been made of it, the procedure presented indicates that it will give satisfactory replication. The method follows:

#### APPARATUS

- (1) *Filter pump*.—Operate on the water system.
- (2) *Filter flasks*.
- (3) *Hirsch funnels*.—3 inch, each fitted with a disc of thin cloth.
- (4) *Kjeldahl nitrogen digester*.—Or equivalent apparatus.
- (5) *Kjeldahl flasks*.
- (6) *Water bath, steam bath*.—Or other low heat.
- (7) *Beakers*.—250 cc., tall-form, lipped. Or use regular style.
- (8) *Rubber stopper*.—No. 11.
- (9) *Filter paper*.—9 cm. folded over above stopper to fit funnel, and capable of retaining the silver chloride precipitate.
- (10) *Buret*.—Calibrated.

#### REAGENTS

- (a) *Silver nitrate*.—Approximately 0.1 *N*, chlorine-free.
- (b) *Potassium iodide*.—Standardize so that 1.0 cc. is equivalent to 1, 2, or 3 mg. of chlorine (chlorine-free).
- (c) *Potassium iodide*.—Similar to reagent (b) but of approximately known strength.
- (d) *Nitric acid*.—Concentrated, chlorine-free.
- (e) *Potassium permanganate*.—6%, chlorine-free.
- (f) *Potassium bi-iodate*.—0.01 *N*, chlorine-free.
- (g) *Starch solution*.—Chlorine-free (5%).
- (h) *Sulfuric acid*.—Ordinary C.P.
- (i) *Potassium sulfate*.
- (j) *Copper*.—Granular, (either metallic or as the sulfate), ordinary C.P.
- (k) *Dilute nitric acid*.—Add 1 cc. to 100 cc. of water.

#### PROCEDURE

Weigh into a 250 cc. beaker a quantity of the sample that will require 25–40 cc. of the standard iodide solution for the final titration. Moisten the sample, heating if necessary; add an excess of the  $\text{AgNO}_3$  solution, 15 cc. of saturated  $\text{KMnO}_4$  solution and 25 cc. of concentrated  $\text{HNO}_3$ ; and boil very gently, or place on a steam or water bath for 15 minutes or until the sample no longer loses color. Dilute to about 200 cc. and heat 10 minutes longer. Cool (it may stand overnight), filter through a previously well-washed filter paper, transferring the entire precipitate to the filter; and wash thoroughly, but not excessively. Use reagent (k) for these washings. Transfer the precipitate with the paper to a Kjeldahl flask and add appropriate quantities of the usual reagents for protein determination (*e.g.*, with 2 grams of grass 20 cc. of sulfuric acid, 8 grams of  $\text{K}_2\text{SO}_4$ , 0.5 gram of  $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$  are adequate). After digestion, cool and add 250 cc. of distilled water.

Prepare the following mixture: To 50 cc. of water add 0.5 cc. of bi-iodate solution, 10 cc. of starch solution,  $\text{AgNO}_3$  solution equivalent to about 25 mg. of chlorine and 0.5 cc. of  $\text{H}_2\text{SO}_4$ , and titrate to the end point with the approximate KI solution, Reagent (c). Add this mixture to the contents of the Kjeldahl flask and titrate with the *Standard* KI solution, Reagent (b).

Make blank determinations and apply the indicated corrections to the calculation of the results. If the corrected value indicates that little or no excess of silver

TABLE 1.—Effect of certain variations in the mixture when titrating with approximately 0.03 N solutions of  $\text{AgNO}_3$  and KI by the Christy-Robson method

	INITIAL VOLUME	VOLUME OF KI REQUIRED						FINAL VOLUME
		1ST	2ND	3RD	4TH	5TH	6TH	
	cc.	cc.	cc.	cc.	cc.	cc.	cc.	cc.
Titrations by Analyst B—5 cc. increments of $\text{AgNO}_3$								
End point established without $\text{AgNO}_3$ .	112	6.03	5.15	5.02				145
End point established with $\text{AgNO}_3$ ....	112	5.70	5.23	4.95				145
End point established with $\text{AgNO}_3$ ....	112	5.75	5.15	5.02				145
End point established with $\text{AgNO}_3$ ....	112	5.86	5.15	5.05	4.92			155
End point established with $\text{AgNO}_3$ ....	112	5.82	5.18	4.99	5.03	4.98	5.05	175
End point established with $\text{AgNO}_3$ ....	9	5.42	5.10	5.00	4.98	5.03	4.98	70
End point established with $\text{AgNO}_3$ ....	212	5.55	5.23	5.15	5.05	5.00	4.97	270
Titrations by Analyst A—5 cc. increments of $\text{AgNO}_3$								
End point established with $\text{AgNO}_3$ ....	112	7.84	5.74	5.03	5.08	5.04		165
End point established without $\text{AgNO}_3$ .	112	5.87	5.25	4.95	5.01	4.90	5.08	175
End point established without $\text{AgNO}_3$ .	112	5.90	5.30	4.95	5.06	4.96	5.05	175
End point established without $\text{AgNO}_3$ .	112	6.02	5.22	4.95	5.08	5.06	5.10	175
End point established without $\text{AgNO}_3$ .	112	6.07	5.23	5.10	5.08	5.00	5.08	175
Titrations by Analyst B—20 cc. increments of $\text{AgNO}_3$								
End point established with $\text{AgNO}_3$ ....	182	20.92	20.08	20.04				300
No end point established before titration.....	32	21.27	20.05	19.87	(ppt. flocculated before end point)			150
Titrations by Analyst A—20 cc. increments of $\text{AgNO}_3$								
End point established without $\text{AgNO}_3$ or gum Ghatti.....	132	21.20	20.03					210
End point established without $\text{AgNO}_3$ but with 10 cc. of 1.5% gum Ghatti.....	132	21.09	20.01	19.98	20.02	20.04	19.98	375
End point established without $\text{AgNO}_3$ but with 1.0 cc. of gum Ghatti....	132	21.15	20.05	20.05	20.00	20.00	19.98	375

NOTE 1.—All titrations were made in the presence of 1 cc. of 1.0% starch solution, 1.0 cc.  $\text{KH}(\text{IO}_3)_2$  solution and acid (1.0 cc. concentrated nitric acid added for each 20 cc. of the initial volume except the ones given in the sixth line of data in which case the initial concentration of acid was re-established after the 3rd increment).

NOTE 2.—With the exception noted the end point was produced in the solution before the first increment of  $\text{AgNO}_3$  solution was added, and with or without the addition of a few drops of  $\text{AgNO}_3$  solution.

TABLE 2.—*Determinations made on a sample of weedy grass, on sugar, and on both of these after chlorine had been added in the form of hydrochloric acid.*

DATA FROM THE APPLICATION OF THE PROCEDURE TO—										
2 GRAMS OF GRASS SAMPLE NO. 213			2 GRAMS OF SUGAR		2 GRAMS OF GRASS PLUS 19.89 MG. OF CHLORINE			2 GRAMS OF SUGAR PLUS 19.89 MG. OF CHLORINE		
NaI <sup>1</sup> TITRATIONS	CHLORINE FOUND <sup>2</sup>		NaI <sup>1</sup> TITRATIONS	ml.	NaI <sup>1</sup> TITRATIONS	ml.	WEIGHT OF CHLORINE FOUND <sup>3</sup>	mg.	NaI <sup>1</sup> TITRATIONS	WEIGHT OF ADDED CHLORINE RECOVERED <sup>4</sup>
	mg.	per cent								
21.68	17.94	0.897		0.15		45.67	37.84	19.94		
21.68	17.94	0.897		0.00		45.52	37.72	19.82		
21.53	17.81	0.890		0.00		45.20	37.45	19.55		
21.63	17.89	0.894		0.05		45.25	37.50	19.60		
21.80	18.04	0.902		0.00		45.35	37.58	19.68		
21.65	17.91	0.896		0.20		45.45	37.66	19.76		
21.60	17.87	0.894		0.32						
21.55	17.83	0.892		0.00						
21.65	17.91	0.896		0.00						
21.58	17.85	0.892		0.00						
Average—21.64		0.895		0.07		45.41	37.63	19.73	23.97	19.83

<sup>1</sup> 1 ml. NaI  $\approx$  0.00083 gram of chlorine.<sup>2</sup> The average blank (0.07 ml.) is used in these calculations.<sup>3</sup> The average chlorine content of the grass ( $\approx$  21.64 ml. NaI) is subtracted from the NaI titration in making these calculations.

nitrate was used to precipitate the silver chloride, repeat the determination, using more  $\text{AgNO}_3$  solution.

Results obtained on a sample of grass are given in Table 2, where it may be seen that of the 19.89 mg. of chlorine added to the sample of grass an average of 99.20 per cent is recovered and that of the same amount added to sugar 99.75 per cent is recovered.

No chlorine-free reagents were prepared for this work; commercial chemicals of reagent quality were used.

The procedure is believed to be convenient to use, to require no apparatus or reagent which is difficult to obtain, to be of rather general application, to be capable of a precision suitable for most purposes, and, (see Table 1) to be but little affected by the volume in which the titration is made. The end point color is very stable and easily seen and is produced by from one to three drops of the 0.03 *N* solutions here employed. Only one standard solution is required, and with it the silver which was combined with the chlorine in the sample is titrated directly.

Further study is needed to determine the best conditions for the various steps in this procedure and time in which to subject the method to critical examination.

It is practically impossible to make an investigation of any kind without the help of colleagues, and sincere thanks are extended to the personnel of all the laboratories at the Animal Husbandry Farm at Beltsville, Md., where the work was done.

It is recommended<sup>1</sup> that the study of the Christy-Robson method for the determination of chlorine in plant materials be continued.

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No report on carbohydrates in plants was given by the associate referee.

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## REPORT ON FORMS OF NITROGEN IN PLANTS

By HUBERT B. VICKERY (Connecticut Agricultural Experiment Station, New Haven, Conn.), *Associate Referee*

A method to determine nitrate nitrogen in plants based on the results of Vickery and Pucher<sup>2</sup> was given in a previous report.<sup>3</sup> As a result of collaborative work,<sup>4</sup> the recommendation was made "that further study be given to the method for the determination of nitrate nitrogen in tobacco." Subsequently a new method was developed and a collaborative study was conducted. The new method is fully described by Pucher, Vickery and Wakeman<sup>5</sup> and has also been published by the Association.<sup>6</sup>

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<sup>1</sup> For report of Subcommittee A and action of the Association, see *This Journal*, 17, 49 (1934).

<sup>2</sup> *Ind. Eng. Chem. Anal. Ed.*, 1, 121 (1929).

<sup>3</sup> *This Journal*, 14, 228 (1931).

<sup>4</sup> *Ibid.*, 15, 516 (1932).

<sup>5</sup> *J. Biol. Chem.*, 97, 605 (1932).

<sup>6</sup> *This Journal*, 16, 474 (1933).



## RESULTS OF COLLABORATIVE STUDY

A specimen of Connecticut shade-grown tobacco was prepared for analysis, and samples were sent to collaborators, together with manuscript copies of the directions. Their reports are summarized in the table. The first three employed the Soxhlet apparatus. Stewart extracted for 20 hours and reports that the extraction procedure is "very satisfactory." Kertesz at first obtained low results (16 hours' extraction) but subsequently extracted for 26 hours. He pointed out the importance of using the apparatus described in the method. Bradshaw used a Soxhlet apparatus that siphoned 15 times an hour and extracted for 14 hours, when the diphenylamine test was found to be negative. His somewhat low results are doubtless to be attributed to incomplete extraction and to the insensitivity of the diphenylamine test as applied in this case. He suggested that the quantity of water to be added to the acidified sample before the reaction is tested at the electrode should be more clearly defined because of possible variations in pH with dilution. The dilution is not, however, of much importance as any reaction within the range pH 0.5-1.0 will give satisfactory results. Mathis conducted the method exactly as described. He reported a 5 per cent variation in the colorimeter readings but founded his final result on an average of 10 readings. Wakeman, of this laboratory carried out the procedure exactly as described. As further evidence of the nitrate content of this specimen he carried out determinations by the

*Collaborative results*

COLLABORATORS	INDIVIDUAL VALUES	AVERAGE
	<i>per cent</i>	<i>per cent</i>
W. D. Stewart	1.07	1.08
	1.08	
	1.10	
Z. I. Kertesz	1.01	1.02
	1.02	
Max A. Bradshaw	0.89	0.905
	0.89	
	0.92	
	0.92	
E. M. Bailey and W. T. Mathis	1.02	1.02
	1.02	
	1.03	
A. J. Wakeman and G. W. Pucher	1.04	1.06
	1.08	
	1.04	
	1.06	
	1.07	
	1.09	
	1.05	
	1.08	

nitron nitrate method described by Pucher, Vickery and Wakeman.<sup>1</sup> Four determinations gave 1.07, 1.07, 1.06 and 1.07 per cent.

The collaborative study has brought out the desirability of adding a few remarks to the original description of the method. The transfer of the mixture of the acidified sample with asbestos may be accomplished more conveniently by making use of a truncated cone constructed of heavy parchment paper. This is held in shape with paper-clips and is impregnated with paraffin. The cone is held in a ring clamped to a ring-stand, and the extraction thimble is supported in a small beaker directly beneath the opening of the cone.

The extraction apparatus originally described is much more efficient than the apparatus of the customary Soxhlet type. If such apparatus is employed it is necessary to allow sufficient extraction time for the ether to siphon back at least 300 times.

The diphenylamine reaction applied to an aqueous extract of the residue in the thimble as a test for complete removal of the nitric acid is not as sensitive as could be desired owing to the color of the solution. The result of a negative test must therefore be accepted with caution.

It is recommended<sup>2</sup> that the method submitted for the determination of nitrate nitrogen in tobacco be adopted as tentative for the determination of nitrate nitrogen in plants.

## REPORT ON SODIUM IN PLANTS

By LILLIAN BUTLER (Michigan Agricultural Experiment Station,  
E. Lansing, Mich.), *Associate Referee*

This study was undertaken for the purpose of finding a short and accurate method for the direct determination of sodium in plant materials to replace the present rather tedious and time-consuming indirect methods.

A review of the literature indicated that the sodium magnesium uranyl acetate method developed by Caley<sup>3</sup> appeared suitable for the determination of small quantities of this element.

The procedure follows.

Ash the sample in a muffle at dull redness, dissolve and remove the phosphate ion, make the solution neutral, and evaporate to a volume of 5 cc. or less. Cool, add 100cc. of magnesium uranyl acetate reagent,<sup>4</sup> place the mixture in a water bath at 20° C., and either stir vigorously for 45 minutes or let stand for 24 hours. Filter with suction and wash with 95 per cent alcohol. Dry at 105–110°C. for 30 minutes, cool, and weigh. As a correction add to the weight of the precipitate 1 mg. for every 5 cc. of 95 per cent alcohol. Weight of sodium magnesium uranyl acetate  $\times 0.0153$  = the sodium.

<sup>1</sup> *Loc. cit.*

<sup>2</sup> For report of Subcommittee A and action of the Association, see *This Journal*, 17, 49 (1934).

<sup>3</sup> Caley and Foulk, *J. Am. Chem. Soc.*, 51, 1664 (1929).

<sup>4</sup> Caley and Sickman, *J. Am. Chem. Soc.*, 52, 4247 (1930).

This method has two distinct advantages over the old methods: (1) The determination can be made in the presence of other radicals with the exception of the phosphate ion, but this can be removed very easily by precipitating as calcium or magnesium phosphate; and (2) because of the high molecular weight of the triple acetate salt, small quantities of sodium can be weighed accurately.

Table 1 gives the results of a few sodium determinations made on synthetic sodium chloride solutions and on samples of grasses and soils. The sodium was determined as the triple acetate and as sodium perchlorate, and in the case of the sodium chloride as sodium sulfate.

TABLE 1.—*Sodium*

SAMPLE	TRIPLE ACETATE	PRESENT	SODIUM MAGNESIUM URANYL ACETATE	NaClO <sub>4</sub> METHOD	Na <sub>2</sub> SO <sub>4</sub> METHOD
			METHOD		
	<i>gram</i>	<i>gram</i>	<i>gram</i>	<i>gram</i>	<i>gram</i>
NaCl Soln.	.6481	.00984	.00992	.00990	.01017
	.6609	.00984	.01011	.00970	.01035
	.0977	.00153	.00150		
Grass No. 207	.0646		.00099	.00070	
	.0714		.00109		
" 208	.0588		.00090	.00075	
	.0566		.00087		
" 209	.0480		.00073	.00065	
	.0455		.00070		
" 210	.0489		.00075	.00065	
	.0476		.00078		
Soil No. 107	.2083		.00319	.00319	
	.1828		.00280	.00330	
" 102	.5508		.00843	.00846	

The data in the table show that it is possible to get results that check very closely among themselves and with other methods.

The Referee suggests that methods for ashing the sample, for extracting the sodium salt from the ash, and for removing the phosphate ion be studied next year. It will be desirable to run this method on a large number of samples of plant material and to obtain data on the determination of the sodium in the presence of large quantities of other elements.

#### POTASSIUM

Incidental to the study of the methods for sodium, some work was also done on the determination of potassium. The perchlorate method compared very favorably with the ordinary platinic chloride method.

The following procedure was followed:

Ash and prepare the material according to the official directions for the determination of sodium and potassium in plant material<sup>1</sup> until a solution of potassium and

<sup>1</sup> *Methods of Analysis*, A.O.A.C., 1930, 106.

sodium nitrate or chloride has been obtained. Then add 3-5 cc. of 60%  $\text{HClO}_4$ .<sup>1</sup> Evaporate to dryness, dissolve in hot water, and again evaporate to dryness. Heat to 350°C. Cool. Weigh if it is desired to obtain the combine perchlorates.<sup>2</sup> Add 10-20 cc. of a solution of anhydrous ethyl acetate and C.P. normal butyl alcohol in equal proportions by volume. Digest near the boiling point for several minutes. Decant into a Gooch crucible. Wash once or twice by decantation. Dissolve in the minimum quantity of water, evaporate to dryness, and extract as before with the acetate alcohol mixture. Filter and wash several times and dry at 350°C. for 15 minutes. Cool and weigh. Potassium perchlorate  $\times 0.28218$  = the potassium content.

TABLE 2.—Potassium

SAMPLE	PRESENT	FOUND	
		$\text{KClO}_4$ , METHOD	$\text{K}_2\text{PtCl}_6$ , METHOD
		gram	gram
KCl	.03314	.03315	
Grass No. 207		.0250	.0250
" 208		.0221	.0232
" 209		.0147	.0138
" 210		.0121	.0137

It was possible to recover the potassium in C.P. potassium chloride, and the results on the grasses indicate that the accuracy of the perchlorate method is as good as that of the platinic chloride method.

RECOMMENDATIONS<sup>3</sup>

It is recommended—

(1) That the study of methods for the determination of sodium in plants be continued.

(2) That the perchlorate method for the determination of potassium in plant materials be studied.

## REPORT ON LIGNIN\*

By MAX PHILLIPS (Bureau of Chemistry and Soils,  
Washington, D. C.), *Referee*

In 1883 Flechsig<sup>1</sup> recorded the observation that when a lignified plant material such as wood is treated with 72 per cent sulfuric acid at ordinary room temperatures, the cellulose and other carbohydrates associated with the lignin are dissolved, and the lignin is left as an insoluble residue. On the basis of this observation, Ost and Wilkenig<sup>2</sup> in 1910 developed a method for the quantitative estimation of lignin. This method was later modified slightly by the chemists<sup>3</sup> of the U. S. Forest Products Labora-

<sup>1</sup> Smith and Ross, *J. Am. Chem. Soc.*, 47, 762 (1925).

<sup>2</sup> Smith and Shead, *J. Am. Chem. Soc.*, 54, 1722 (1932).

<sup>3</sup> For report of Subcommittee A and action of the Association, see *This Journal*, 17, 49 (1934).

\* Contribution No. 235 from the Color and Farm Waste Division, Bureau of Chemistry and Soils, U. S. Department of Agriculture, Washington, D. C.

<sup>1</sup> *Z. physiol. Chem.*, 7, 523 (1883).

<sup>2</sup> *Chem. Z.*, 34, 461 (1910).

<sup>3</sup> *Ind. Eng. Chem.*, 14, 933 (1922); *Paper Trade J.*, 87, No. 25, 59 (1928).

tory at Madison, Wisconsin. According to these modified directions the sample of dried wood, previously extracted either with ether or with a minimum boiling solution of alcohol and benzene, is treated with 72 per cent sulfuric acid in the proportion of 20 cc. of acid to 1 gram of sample and allowed to remain at room temperatures for 16 hours. The resulting reaction mixture is diluted with a sufficient quantity of water to make approximately a 3 per cent acid solution and boiled for 2 hours in order to complete the hydrolysis of the carbohydrates. The lignin is then filtered off, dried at 105°C., and weighed.

The Forest Products Laboratory method was modified further by Peterson, Walde and Hixon,<sup>1</sup> who suggested that unless the temperature during the hydrolysis of the sample with the 72 per cent sulfuric acid is carefully controlled, insoluble reversion products are formed from the carbohydrates, with the result that high values for lignin are obtained. They accordingly recommended that the temperature during the hydrolysis with the strong acid be maintained between 4° and 15°C. However, they failed to take into consideration the fact that insoluble nitrogenous products are also formed as a result of the hydrolysis and are weighed along with the lignin.

In 1913 Willstätter and Zechmeister<sup>2</sup> recorded the important observation that although ordinary concentrated hydrochloric acid will not dissolve cellulose at ordinary room temperatures, at least to an appreciable extent, fuming hydrochloric acid, that is to say an acid solution containing 42–43 per cent HCl, will dissolve cellulose readily in the cold. Based upon this principle, a method for the quantitative estimation of lignin was developed by the Referee.<sup>3</sup> This method is generally recognized as more accurate than any of the methods specifying strong sulfuric acid for the hydrolysis of the cellulose and associated carbohydrates.<sup>4</sup> One disadvantage of the method is that it is more laborious and more difficult to carry out, and another objection arises from the fact that fuming hydrochloric acid is rather an unpleasant substance to handle in the laboratory. In the determination of lignin in wood, however, the difference in results obtained with the two methods is so small that the 72 per cent sulfuric acid method is usually employed.

Schwalbe<sup>5</sup> endeavored to apply a combination of the Willstätter and the Flechsig principles to the determination of lignin. He uses a mixture of 72 per cent sulfuric acid and hydrochloric acid (d. 1.07) and considers that the hydrochloric acid gas generated by the action of the strong sulfuric acid upon the hydrochloric acid is helpful in the hydrolysis of the cellulose and associated carbohydrates.

During recent years a renewed interest in the lignin problem has been

<sup>1</sup> *Ind. Eng. Chem. Anal. Ed.*, **4**, 216 (1932).

<sup>2</sup> *Ber.*, **46**, 2401 (1913).

<sup>3</sup> *This Journal*, **15**, 118 (1932).

<sup>4</sup> *Paper Trade J.*, **96**, No. 4, 30 (1933).

<sup>5</sup> *Papier-Fabr.*, **23**, 174 (1925).

TABLE 1.—*Lignin by the fuming hydrochloric acid and Schwalbe methods*  
 (Results, except for oat hulls, were calculated on basis of original dry material. The results for oat hulls were calculated on the basis of the extracted and dried material.)

PLANT MATERIAL	WEIGHT OF SAMPLE (ORIGINAL DRY MATERIAL)		EXTRACTED BY ALCOHOL- BENZENE AND BY HOT WATER	WEIGHT OF CRUDE LIGNIN		N IN CRUDE LIGNIN	ASH IN CRUDE LIGNIN	WEIGHT OF LIGNIN CORRECTED FOR ASH AND PROTEIN		LIGNIN (CALCULATED ON ORIGINAL DRY MATERIAL)	
	(A)	(B)		(A)	(B)			(A)	(B)	(A)	(B)
grams				gram		per cent		gram		per cent	
Fuming HCl Method											
Corn Cobs	1.4052	1.4149	6.24	0.1676	0.1646	0.89	2.98	0.1534	0.1500	10.91	10.64
Wheat Straw	1.1088	1.1088	9.82	0.1760	0.1754	0.65	6.02	0.1584	0.1578	14.28	14.23
Spruce Wood	1.0495	1.1385	6.15	0.2903	0.3125	0.11	None	0.2885	0.3107	27.49	27.29
Wheat Bran	1.4317	1.3287	17.77	0.1195	0.1120	2.98	1.08	0.0963	0.0903	6.72	6.79
Timothy Hay	1.3829	1.3829	27.69	0.1748	0.1784	1.28	11.55	0.1408	0.1436	10.21	10.38
Corn Stalks	1.1418	1.1418	12.42	0.1938	0.1952	1.60	7.63	0.1598	0.1611	14.00	14.10
Oak Leaves	1.4045	1.0343	23.81	0.4223	0.4005	1.39	1.83	0.3780	0.3584	26.91	26.40
Oat Hulls	1.0248	0.9537	—	0.1724	0.1550	None	25.00	0.1293	0.1163	12.61	12.19
Schwalbe Method											
Corn Cobs	1.0665	1.0665	6.24	0.1369	0.1424	1.41	2.37	0.1217	0.1265	11.41	11.86
Wheat Straw	1.1088	1.1088	9.82	0.2016	0.2009	0.97	5.97	0.1774	0.1768	15.99	15.94
Spruce Wood	1.0655	1.0655	6.15	0.3112	0.3071	0.18	0.35	0.3067	0.3026	28.78	28.40
Wheat Bran	1.2161	1.2161	17.77	0.1083	0.1058	3.44	1.60	0.0834	0.0814	6.85	6.69
Timothy Hay	1.3829	1.3829	27.69	0.1947	0.1927	1.98	11.62	0.1481	0.1465	10.70	10.59
Corn Stalks	1.1418	1.1418	12.42	0.2170	0.2075	1.07	7.85	0.1855	0.1774	16.24	15.53
Oak Leaves	1.3125	1.3125	23.81	0.4032	0.3990	1.75	1.52	0.3530	0.3493	26.89	26.61
Oat Hulls	1.0000	1.0000	—	0.1885	0.1816	0.42	21.64	0.1429	0.1376	14.29	13.76

TABLE 2.—*Lignin by Peterson-Walde-Hixon and regular 72 per cent H<sub>2</sub>SO<sub>4</sub> methods*

(Results, except for oat hulls, were calculated on basis of original dry material. The results for oat hulls were calculated on the basis of extracted and dried material.)

PLANT MATERIAL	WEIGHT OF SAMPLE (ORIGINAL DRY MATERIAL)		EXTRACTED BY ALCOHOL- BENZENE AND BY HOT WATER	WEIGHT OF CRUDE LIGNIN		N IN CRUDE LIGNIN	ASH IN CRUDE LIGNIN	WEIGHT OF LIGNIN CORRECTED FOR ASH AND PROTEIN		LIGNIN (CALCULATED ON ORIGINAL DRY MATERIAL)	
	(A)	(B)		(A)	(B)			(A)	(B)	(A)	(B)
per cent											
grams				gram				per cent			
Peterson-Walde-Hixon Method											
Corn Cobs	1.1600	1.1651	6.24	0.1667	0.1657	1.62	2.93	0.1450	0.1442	12.50	12.37
Wheat Straw	1.2208	1.1316	9.82	0.2495	0.2324	1.00	5.37	0.2206	0.2055	18.07	18.16
Spruce Wood	1.0869	1.1052	6.15	0.3235	0.3315	0.10	0.06	0.3213	0.3293	29.56	29.79
Wheat Bran	1.2516	1.3041	17.77	0.1673	0.1703	5.16	1.25	0.1114	0.1133	8.90	8.68
Timothy Hay	1.4476	1.4769	27.69	0.2435	0.2468	2.57	11.04	1.1775	0.1800	12.26	12.18
Corn Stalks	1.1611	1.1514	12.42	0.2363	0.2317	1.41	8.25	0.1960	0.1922	16.88	16.69
Oak Leaves	1.3751	1.3601	23.81	0.4487	0.4358	2.07	1.44	0.3842	0.3733	27.93	27.15
Oat Hulls	1.0658	1.0237	—	0.2809	0.2692	0.57	18.68	0.2184	0.2095	20.49	20.46
Regular 72% H <sub>2</sub> SO <sub>4</sub> Method											
Corn Cobs	1.7436	1.1892	6.24	0.4825	0.3322	0.76	1.32	0.4533	0.3121	25.99	26.24
Wheat Straw	1.1219	1.1219	9.82	0.2620	0.2561	0.92	4.29	0.2358	0.2304	21.01	20.53
Spruce Wood	1.0737	0.8697	6.15	0.3332	0.2691	0.30	0.33	0.3260	0.2632	30.36	30.26
Wheat Bran	1.2161	1.2161	17.77	0.1907	0.1939	4.23	0.51	0.1394	0.1417	11.46	11.65
Timothy Hay	1.4949	1.3638	27.69	0.3460	0.3157	1.45	8.01	0.2870	0.2618	19.19	19.19
Corn Stalks	1.2194	1.4684	12.42	0.2862	0.3413	1.19	6.24	0.2472	0.2947	20.27	20.06
Oak Leaves	1.3319	1.2518	23.81	0.4089	0.3876	1.67	1.49	0.3603	0.3414	27.05	27.27
Oat Hulls	1.0000	1.0000	—	0.3668	0.3677	0.33	13.21	0.3109	0.3116	31.09	31.16

shown by agricultural chemists, and it is now generally recognized that lignin is an important factor in the formation of soil organic matter or humus. In order to study the microbiological decomposition of lignin and also to determine the effect of lignin on the digestibility of feeds and fodders, it is necessary to employ analytical methods. Accordingly, some investigators have applied indiscriminately the methods developed in connection with chemical studies of wood to the determination of lignin in such materials as cereal straws, corn stalks, corn cobs, hulls, and hay, before determining whether these methods can be used successfully on these materials.

In this report analytical data are presented on the quantitative estimation of lignin by four different methods, namely: (1) the fuming hydrochloric acid method of Willstätter and Zechmeister;<sup>1</sup> (2) the regular 72 per cent sulfuric acid method, or the Forest Products Laboratory method;<sup>1</sup> (3) the modified 72 per cent sulfuric acid method of Peterson, Walde and Hixon;<sup>1</sup> and (4) the Schwalbe method.<sup>1</sup> Eight different plant materials, which had previously been extracted with 1:2 alcohol-benzene solution and then with hot water, were analyzed for lignin and the results (except in the case of oat hulls) were calculated on the basis of original dry material. In the case of oat hulls, the results were calculated on the basis of the extracted and dried material. In all cases proper deductions were made for the ash and crude protein ( $N \times 6.25$ ) in the "lignin" residues obtained. The results obtained are recorded in Tables 1 and 2, and summarized in Table 3.

TABLE 3.—*Lignin in plant materials (Summary)*

PLANT MATERIAL	PERCENTAGE OF LIGNIN FOUND BY—			
	FUMING HCl METHOD	SCHWALBE METHOD (72% H <sub>2</sub> SO <sub>4</sub> +14% HCl)	PETERSON-WALDE- HIXON METHOD	REGULAR 72% H <sub>2</sub> SO <sub>4</sub> METHOD
Corn Cobs	10.77	11.63	12.43	26.11
Wheat Straw	14.25	15.96	18.11	20.77
Spruce Wood	27.39	28.59	29.67	30.31
Wheat Bran	6.75	6.77	8.79	11.55
Timothy Hay	10.29	10.64	12.22	19.19
Corn Stalks	14.05	15.88	16.78	20.16
Oak Leaves	26.65	26.75	27.54	27.16
Oat Hulls	12.40	14.02	20.47	31.12

It will be observed from the results that, as compared with the fuming hydrochloric acid method, the 72 per cent sulfuric acid method (Forest Products Laboratory method) gives decidedly less satisfactory results than either the Schwalbe method or the Peterson-Walde-Hixon method. The last-named method, although better than the Forest Prod-

<sup>1</sup> *Loc. cit.*



ucts Laboratory method, is decidedly inferior to the Schwalbe method. In all cases higher results were obtained by the Forest Products Laboratory method, the Peterson-Walde-Hixon method, and the Schwalbe method than by the fuming hydrochloric acid method. The difficulty apparently arises from the fact that in the three methods first mentioned, there is incomplete hydrolysis of the carbohydrates or insoluble reversion products are formed, with the result that too high values for lignin are obtained. In the case of spruce wood and oak leaves the percentages of lignin found by the four methods agree much better than those found for the other plant materials. It is clear from the data presented that the percentages of "lignin" found in such agricultural materials as corn cobs, wheat straw, wheat bran, timothy hay, corn stalks, and oat hulls, by either the Forest Products Laboratory method or by the Peterson-Walde-Hixon method are absolutely worthless. The results obtained by the Schwalbe method, although somewhat higher than those obtained by the fuming hydrochloric acid method, are nevertheless of the same general order of magnitude. It would seem that this method is entitled to further study.

It is recommended<sup>1</sup> that further studies be made of the Schwalbe method and the fuming hydrochloric acid method for the determination of lignin.

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A report of progress was presented by the Referee on Enzymes.

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<sup>1</sup> For report of Subcommittee A and action of the Association, see *This Journal*, 17, 50 (1934).

## CONTRIBUTED PAPERS

### VOLATILE OIL IN CARDAMOM SEED<sup>1</sup>

By J. F. CLEVINGER (U. S. Food and Drug Administration,  
New York, N. Y.)

During the past four years many of the importations of cardamoms in New York have been analyzed for the yield of volatile oil, and determinations have also been made to ascertain some of the physical and chemical characteristics of these oils.

Cardamoms are usually imported from Ceylon or India. From Ceylon and India they are generally in the form of fruit of two types. One type, large, smooth and white, is invoiced as bleached cardamom; the other, smaller, brownish green in color and somewhat shriveled is usually invoiced as green cardamom. Cardamom seeds are also imported from these countries, and seeds (but no fruit) are imported from Guatemala.

Cardamom seed was separated from the fruits of both the bleached and green cardamoms, and the percentages of husks and seed were determined in several instances. The results, varying from 65 to 75 per cent, indicate that the percentage of seed in the husks is practically the same for both types of the fruit. In a few determinations for oil on hulls with a small proportion of immature seed (which are removed only with difficulty), yields of volatile oil up to 1 per cent were obtained. The physical and chemical characteristics of this oil were similar to those of the oil distilled from the seed. An examination of husks from which all the immature seeds had been carefully removed yielded less than 0.2 per cent of volatile oil.

Representative results obtained by the method outlined by Clevenger<sup>2</sup> on cardamom seed from fruits of bleached and green cardamoms and from cardamom seed as imported are given in the following table. This work was made possible through the cooperation of O. C. Kenworthy of the New York Laboratory.

Cardamom seed is official in U.S.P.X., which requires that it be "recently removed from the capsule." As it will also be official in U.S.P. XI, the following examinations were made to determine the significance of this requirement.

To determine the effect of the husk on retention of the volatile oil, some uniformly mixed green cardamoms were divided into two portions. One portion, designated as (a), was shelled at one time, and determinations were made at recorded intervals. The other portion, designated as (b), was assayed at the same intervals, but the shells were removed from

<sup>1</sup> Presented at the Annual Meeting of the Association of Official Agricultural Chemists, November, 1933.

<sup>2</sup> *J. Am. Pharm. Assoc.*, 17, 345 (1928); *This Journal*, 16, 557 (1933); 17, 70 (1934).

NO.	YIELD v/w	SP. GR. 20°/20°C.	OP. ROT. 20° C.	REF. IND. 20° C.	ACID NO.
<i>Oil from cardamom seed from bleached cardamoms</i>					
1	6.4	0.932	+33.4	1.466	2.6
2	5.2	0.934	+36.7	1.466	3.5
3	10.7	0.925	+28.2	1.465	2.1
4	8.3	0.922	+27.0	1.461	2.4
5	9.6	0.926	+27.3	1.465	2.5
6	5.3	0.938	+32.8	1.467	3.2
7	7.5	0.935	+29.7	1.465	2.9
8	6.0	0.935	+34.2	1.465	1.8
9	8.4	0.930	+31.3	1.467	2.3
10	11.2	0.931	+33.0	1.466	4.8
<i>Oil from cardamom seed from green cardamoms</i>					
1	6.6	0.923	+32.7	1.461	2.5
2	10.5	0.926	+32.3	1.463	1.5
3	8.9	0.923	+22.6	1.461	2.5
4	10.1	0.930	+27.7	1.464	3.4
5	8.2	0.928	+23.8	1.462	1.6
6	11.2	0.925	+26.6	1.464	2.1
7	11.0	0.925	+20.1	1.464	1.7
8	9.0	0.926	+26.3	1.461	2.1
9	9.5	0.929	+25.2	1.462	1.1
10	6.6	0.930	+21.1	1.461	2.8
<i>Oil from cardamom seed (India)</i>					
1	3.4	0.925	+25.6	1.461	—
2	5.2	0.930	+26.3	1.463	3.2
3	5.9	0.930	+20.7	1.462	2.0
4	8.0	0.923	+27.2	1.462	1.0
5	6.0	0.927	+29.3	1.463	3.8
6	4.4	0.931	+36.7	1.464	3.9
7	4.4	0.926	+31.8	1.463	4.3
8	3.5	0.932	+34.5	1.467	4.5
<i>Oil from cardamom seed (Guatemala)</i>					
1	6.0	0.927	+32.5	1.464	—
2	3.5	0.925	+32.2	1.467	—
3	4.0	0.929	+31.5	1.465	5.6
4	3.6	0.926	+34.6	1.463	0.8
5	4.0	0.929	+30.7	1.464	3.5
6	5.7	0.923	+36.1	1.466	3.2
7	6.4	0.930	+27.7	1.464	1.2
8	8.6	0.924	+30.2	1.464	1.0
9	4.1	0.932	+35.6	1.465	1.0

the sample at the time of each determination. The entire lot (green cardamom fruit and seed) was stored in the laboratory in open shallow pans during the period of the experiment. The results follow.

DATE	PORTION	MOISTURE	YIELD v/w	SP. GR. 20°/20° C.	OP. ROT. 20° C.	REF. IND. 20° C.	ACID NO.
		<i>per cent</i>					
1-5-33	a	7.0	10.6	0.930	+29.1	1.463	1.8
2-24-33	b	7.0	10.5	0.930	+30.4	1.462	2.3
"	a	7.0	9.1	0.930	+31.4	1.462	2.0
5-24-33	b	7.5	10.1	0.926	+29.0	1.462	2.0
"	a	7.5	8.3	0.928	+29.0	1.463	1.9
7-25-33	b	7.5	10.3	0.926	+28.7	1.461	2.6
"	a	7.5	7.8	0.924	+29.7	1.461	2.5
9-11-33	b	9.8	9.6	0.930	+30.4	1.464	2.0
"	a	9.8	7.3	0.929	+29.7	1.463	2.8

A determination of the saponification value of cardamom oil also was made. Approximately 1.8 gram portions of an oil were treated with equal volumes (20 cc.) of 0.5 *N* alcoholic potassium hydroxide for periods varying from 30 minutes to 4 hours. The values obtained are tabulated below:

Portion	1	2	3	4	5	6	7	8
Time of Saponification	30 min.	1 hr.	1½ hrs.	2 hrs.	2½ hrs.	3 hrs.	3½ hrs.	4 hrs.
Saponification No.	86.8	120.5	135.9	142.1	152.6	152.3	154.2	149.8

It is evident from the above results that cardamom oil requires approximately 3 hours for saponification.

#### CONCLUSIONS

(1) For all practical purposes the husks from cardamom fruits may be considered inert.

(2) Seed from green cardamom yields on the average appreciably more volatile oil than does seed from bleached cardamom.

(3) Cardamom seed, imported as such, yields on the average less volatile oil than that recently removed from the husks. This is due, no doubt, to the lack of the protection of the husks.

(4) The loss of volatile oil in husk-protected seed is comparatively small during eight months.

(5) The loss of volatile oil in cardamom seed removed from the shells is considerable, amounting to approximately 30 per cent in eight months.

(6) The physical and chemical characteristics of the volatile oils obtained are essentially the same.

(7) The time required for complete saponification of cardamom oil is approximately 3 hours.

## A MODIFIED SULFOCYANATE PROCEDURE FOR THE DETERMINATION OF SMALL QUANTITIES OF IRON

By HARLEY A. DANIEL and HORACE J. HARPER (Oklahoma Agricultural Experiment Station, Stillwater, Oklahoma)

In a recent investigation conducted in this laboratory, an accurate method was needed for the determination of small quantities of iron. Previous studies had indicated that the fading of the color of ferric sulfocyanate in aqueous solutions could produce a serious error in this determination. Consequently the method outlined by Stugart<sup>1</sup> was selected for trial, as isoamyl alcohol extracts the ferric sulfocyanate complex from other substances which may be present in aqueous solutions and may interfere with the accuracy of the determination.

The results obtained with this procedure, however, were not satisfactory. In many instances complete recovery of known quantities of iron added to samples of forage could not be obtained. On standing the red color frequently changed to an orange shade, and accurate comparisons were not always possible. As the first series of experiments with isoamyl alcohol was made in hot weather when the laboratory temperatures were always above 30°C., another experiment was conducted to study the stability of the color in isoamyl alcohol at 15, 25, and 35°C. Erratic data were obtained even when isoamyl alcohol, b.p. 130–132°C., was used. Fading of the color occurred in all solutions, and the intensity of the color varied with the temperature of the solution. When a considerable quantity of calcium salts was present in the solutions, yellowish tints appeared and made accurate comparison difficult.

As many of the samples analyzed for iron had a high calcium content, a third experiment was conducted to determine the effect of calcium on the recovery of iron by the sulfocyanate method in hydrochloric acid and in nitric acid solution. Hydrochloric acid solutions, as recommended by Winter,<sup>2</sup> were compared with nitric acid solutions containing the same quantities of calcium and iron, and on final dilution about 1 per cent of the acid. The results of these comparisons are given in Table 1.

As the calcium content of solutions increased, the total amount of iron recovered decreased when hydrochloric acid was used, but a complete recovery of iron was obtained in the nitric acid solutions. The error due to calcium salts was not serious in the hydrochloric acid solutions when less than 10 mg. was present in 100 cc. When larger quantities of calcium salts were present, the recovery of iron was lowered consistently. This condition would occur in forage which frequently contains from 2 to 3 per cent of total calcium.

<sup>1</sup> *Ind. Eng. Chem. Anal. Ed.*, 3, 390 (1931).

<sup>2</sup> *This Journal*, 14, 216 (1931).

As Scott<sup>1</sup> recommended the use of sulfuric acid as a solvent in the determination of small quantities of iron by the sulfocyanate method, a comparison was made of a series of solutions of known iron content, treated with varying quantities of nitric, hydrochloric, and sulfuric acid. It was found that the iron color fades rapidly in hydrochloric and sulfuric acid solutions, but very little when nitric acid is used. The sulfuric acid was also found to be objectionable when a considerable amount of calcium is present because calcium sulfate tends to precipitate on dilution unless a high concentration of the acid is maintained. The use of nitric acid according to Scott is not recommended because with sulfocyanates it gives a color that may be mistaken for iron.

TABLE 1.—*Effect of calcium on the recovery of known quantities of iron in hydrochloric and in nitric acid solutions*

SAMPLE NO.	CALCIUM ADDED	RECOVERY OF IRON*	
		HYDROCHLORIC ACID	NITRIC ACID
	mg. per 100 cc.	per cent	per cent
1	None	100	100
2	2.0	98	100
3	4.0	96	100
4	8.0	96	100
5	12.0	88	100
6	16.0	88	100
7	20.0	84	100
8	30.0	80	100

\* 0.05 mg. of Fe added to all solutions. Total volume 100 cc.

Zega<sup>2</sup> used nitric acid in the determination of iron in water and recommended that solutions contain one per cent of nitric acid when the sulfocyanate is added. Walker<sup>3</sup> states that ordinary nitric acid gives a red color with thiocyanate, but that the color is due to the presence of nitrous acid, which may be oxidized by the addition of hydrogen peroxide. In this study it was found that solutions containing potassium sulfocyanate and 1 per cent of nitric acid developed no color on standing for 12 hours at room temperature. High concentrations of the same acid developed a red color in potassium sulfocyanate solutions in a few minutes.

The fading of the ferric sulfocyanate is probably due to the reducing action of products formed from the slow decomposition of sulfocyanic acid in dilute acid solutions. The odor of sulfides is often prominent when hydrochloric or sulfuric acid is used to acidify the solutions. It was found that when potassium sulfocyanate remains in contact with hydrochloric

<sup>1</sup> Standard Methods of Chemical Analysis, p. 261. D. Van Nostrand Co., New York, (1927).

<sup>2</sup> Chem. Ztg., 17, 1564 (1893).

<sup>3</sup> Analyst, 50, 279 (1925).

acid or sulfuric acid for 12 hours and then a known quantity of iron is added, the amount of iron recovered is very low as compared with similar solutions treated with nitric acid. In the presence of nitric acid, even though the concentration may be low, ferric iron is not reduced to the ferrous form by the decomposition of sulfocyanic acid. A comparison of these treatments is given in Table 2.

TABLE 2.—*Recovery of iron in acid solutions which had been in contact with potassium sulfocyanate for 12 hours before the iron was added\**

NO.	ACID USED	CONCENTRATION	IRON RECOVERED AT VARIOUS TEMPERATURES		
			19°C.	23°C.	32°C.
		per cent	mg.	mg.	mg.
1	H <sub>2</sub> SO <sub>4</sub>	0.5	.070	.070	.065
2	"	3.0	.070	.065	.060
3	"	10.0	.070	.060	.050
4	HCl	0.5	.090	.085	.065
5	"	3.0	.085	.080	.065
6	"	10.0	.085	.080	.050
7	HNO <sub>3</sub>	0.5	.100	.100	.105
8	"	1.0	.100	.100	.120†
9	"	2.0	—‡	—‡	—‡

\* 0.1 mg. of iron was added to all samples.

† Slight color in solution before iron was added.

‡ Color developed in 12 hours without the addition of iron.

Further studies on the use of nitric acid as a solvent indicate that 2 per cent of this acid can be used if the temperature is less than 25°C., and no error due to the color produced by oxides of nitrogen will occur. Even if a slight color should develop from the use of nitric acid, this error may be corrected by making a blank determination on reagents used in the analysis. Strong solutions of nitric acid are not needed in this determination as low concentrations of iron salts will not hydrolize so long as the pH value of the solution is less than 2.0; consequently there is no reason for the use of a high concentration of nitric acid, which might produce a color with the sulfocyanate reagent in the absence of iron.

Elvehjem and Hart<sup>1</sup> used nitric acid as recommended by Walker<sup>2</sup> and obtained better results than with hydrochloric acid in the analysis of materials like cabbage, the ash of which has a relatively high phosphate content, but they could not use it in the analysis of milk, the ash of which, in relation to the iron, has an excessive phosphate content. Stugart<sup>3</sup> has shown that pyrophosphates can readily be changed to orthophosphates by heating in dilute acid solution; consequently phosphates should not interfere in the proposed method.

<sup>1</sup> *J. Biol. Chem.*, 67, 43 (1926).

<sup>2</sup> *Loc. cit.*

<sup>3</sup> *Loc. cit.*

The procedure proposed by the writers for forage and grain follows:

Weigh 1 or 2 grams of oven-dried material into a porcelain evaporating dish and ignite to dull redness to destroy organic matter. If a black residue remains, moisten the ash with water; add 2 cc. of HCl and 1 cc. of HNO<sub>3</sub>; evaporate to dryness, re-ignite, and cool. Treat the ash with 10 cc. of 3*N* hydrochloric acid, evaporate to dryness at a temperature of 110 to 125°C., and continue heating to dehydrate silica, if present. Then add 20 cc. of 3 *N* HCl, heat for 20 minutes, dilute to 100 cc., filter, and take an aliquot containing 0.05–0.1 mg. of iron for analysis. (A 10 cc. aliquot is usually satisfactory.) Place the aliquot in a 250 cc. beaker, add 10 cc. of 3 *N* HNO<sub>3</sub>, and evaporate to dryness at 100°C. Add another 10 cc. of HNO<sub>3</sub> and evaporate again to remove any chlorides that remain. Treat the residue with 20 cc. of 0.5 *N* HNO<sub>3</sub> and heat for 10 minutes. Dilute with 70 cc. of distilled water, add 10 cc. of 20% KCNS solution, and mix thoroughly. Allow the color to develop for 5 minutes, and then compare in 100 cc. Nessler tubes with standard iron solutions that contain from 0.02 to 0.1 mg. of iron in 100 cc.

A comparison was made of the procedure described and the procedure recommended by Winter, with 24 different samples of forage having a wide variation in iron content. One sample only gave higher results by the hydrochloric acid procedure; two samples yielded the same quantity of iron by both methods; and 21 samples gave higher results by the nitric acid procedure. The average iron content for all samples was 29 per cent higher when the nitric acid solutions were used than when similar unknown solutions and standards prepared with hydrochloric acid and potassium sulfocyanate were employed. The low values for iron obtained from solutions treated with hydrochloric acid are probably due to the effect of calcium chloride, as many of these samples were high in total calcium. These results agree with data obtained by Weber,<sup>1</sup> who reported that alkaline earth chlorides, especially calcium chloride, interfere with the formation of ferric sulfocyanate complex, but that alkaline earth nitrates have very little effect on this reaction.

This procedure can be adapted to the determination of small quantities of iron in either liquids or solids, subject to its limitation in the presence of certain inorganic salts such as silver, copper, cobalt, and mercury.

#### SUMMARY

A detailed study of methods for the colorimetric determination of small quantities of iron was made. Erratic results were obtained with the isoamyl alcohol modification of the sulfocyanate method, and fading of the ferric sulfocyanate solutions occurred at all temperatures. The presence of calcium salts also caused undesirable colors.

The color of the ferric sulfocyanate complex is intense and does not fade appreciably in dilute nitric acid solutions, but it does fade in solutions containing hydrochloric or sulfuric acid. The presence of large quantities of calcium chloride interferes with the accuracy of the sulfo-

<sup>1</sup> *Chem. News.*, 47, 165 (1883).



cyanate method in hydrochloric acid solution, but does not produce any appreciable effect when the calcium is in the form of calcium nitrate and nitric acid is used as a solvent.

The procedure outlined for the determination of small quantities of iron in forage and grain is not affected by the presence of large quantities of calcium salts or pyrophosphates, and the error due to fading of the color is practically eliminated.

## THE IRON, COPPER, AND MANGANESE CONTENT OF CALIFORNIA PRUNES

By L. G. SAYWELL, W. H. DIETZ, and P. D. ROBERTSON (Fruit Products Laboratory, University of California, Berkeley, Calif.)

Recent researches in nutrition indicate the value of traces of iron, copper, and manganese in food. Many studies (3, 4, 6, 7, 15, 16, 18) of the rôle of iron and copper have been reported. Considerable attention has been given to the value of vegetables (7, 15), and Whipple (18) has studied dried prunes. Results indicate that prunes may be an important factor in the diet in relation to red blood cell regeneration and that this value is due to their iron and copper content. The nutritive value of manganese has also received attention. Studies by McCollum and Orent (9, 12) and by Hart and his co-workers (5) show that elimination of manganese from an otherwise adequate ration was followed by serious degenerative deficiencies in the productive functions of both sexes of the animal.

As a result of the above-mentioned study (18) of the nutritional value of prunes and because the published reports of the iron, copper, and manganese content of prunes are meager (8, 13, 14) and generally of single samples, it appeared desirable to secure analyses of representative samples from the important prune-growing districts of California. In addition, information could be obtained as to the variations in samples from the different districts as well as from a given district, which is important owing to the climatic differences of districts.

Five samples were obtained for each of the three principal prune-growing districts. The fruit used was free from any type of spray or fertilizer materials containing iron, copper or manganese. The methods of analysis were those used by previous investigators. Iron was determined by the thiocyanate method of Stugart (17) and copper by the copper-pyridine-thiocyanate method of Gebhardt and Sommer (2). Manganese was determined by the persulfate method of Newcomb and Sankaran (11, 1), with wetting of the first ash with concentrated sulfuric acid, heating to dryness, and repetition of the acid treatment (1). The standard manganese solution was prepared according to the method of McHargue (10). Ashing was accomplished in platinum dishes in an electric muffle regulated at 565°C.

The applicability of the method to the analysis of fruit products such as dried prunes was determined by a series of recovery experiments on known quantities of the metals being determined. The procedure was to ash a suitable portion of a sample, usually 25–100 grams, determine the metal content, and to repeat the method with similar portions of sample to which had been added approximately 25 and 50 per cent, respectively, of the original metal content. The data are presented in Table 1.

TABLE 1.—*Iron, copper and manganese recovery from prune flesh*  
(Basis of 100 grams of flesh of 20% moisture content.)

SAMPLE	IRON			
	PRESENT	ADDED	DETERMINED	RECOVERY
	mg.	mg.	mg.	per cent
SV1	4.09	1.00	5.06	99.4
	4.09	2.00	6.07	99.7
NS5	3.27	1.00	4.26	99.8
	3.27	2.00	5.25	99.6
SC4	6.02	1.50	7.48	99.5
	6.02	3.00	9.05	100.1
COPPER				
SV1	0.213	0.050	0.260	98.9
	0.213	0.100	0.311	99.5
NS5	0.224	0.050	0.272	99.3
	0.224	0.100	0.323	99.7
SC4	0.382	0.100	0.480	99.6
	0.382	0.200	0.577	99.1
MANGANESE				
SV1	0.351	0.100	0.449	99.6
	0.351	0.200	0.549	99.6
NS5	0.388	0.100	0.485	99.4
	0.388	0.200	0.584	99.3
SC4	0.530	0.150	0.673	99.0
	0.530	0.250	0.775	99.4

All determinations on the samples from the different districts were run in duplicate or triplicate, the average of closely agreeing duplicates being reported. As previously, all results were calculated to the common basis of a fleshy edible portion of 20 per cent moisture content. The data are given in Table 2.

From the results given in Tables 1 and 2 it would appear that there is considerable variation in the iron, copper and manganese content of prunes within a given district, as well as in different districts. All the values vary within figures of the same magnitude, nevertheless percentage differences may be large.

The actual amount of the individual minerals per 100 grams of edible portion compares well with that of many of the common foods, and with

TABLE 2.—*Iron, copper and manganese of California prunes (edible portion)*  
(Basis of 20% moisture.)

SAMPLE NO.	IRON	COPPER	MANGANESE
	<i>per cent</i>	<i>per cent</i>	<i>per cent</i>
SV1	.00409	.00021	.00035
SV2	.00446	.00021	.00042
SV3	.00558	.00028	.00045
SV4	.00508	.00025	.00056
SV5	.00395	.00027	.00054
Av.	.00463	.00024	.00046
NS1	.00378	.00023	.00031
NS2	.00303	.00038	.00050
NS3	.00374	.00038	.00031
NS4	.00301	.00026	.00043
NS5	.00327	.00022	.00039
Av.	.00337	.00031	.00039
SC1	.00426	.00041	.00048
SC2	.00575	.00028	.00047
SC3	.00454	.00029	.00055
SC4	.00602	.00038	.00053
SC5	.00493	.00033	.00051
Av.	.00437	.00034	.00047

many of those well known for their mineral content. Peterson and Elvehjem (13) reported the iron content of many common foods, the values ranging from 0.0004 to 0.006 per cent. Lindow, Elvehjem and Peterson (8) reported the copper content of presumably a single sample of prunes as 0.0004 per cent (40 per cent moisture), which is somewhat higher than the average result reported here. It is evident that the relative copper content of prunes is above the average of that of similar foods. From the data of Peterson and Skinner (14) on 83 food materials it is evident that on the fresh basis prunes contain equivalent or larger quantities of manganese than do many food materials, including the average of other dried fruits, green leafy vegetables, roots and tubers, non-leafy vegetables, fresh fruits, poultry and dairy products, and fish and sea foods.

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## A CRITICAL STUDY OF THE MUNSON-WALKER METHOD FOR REDUCING SUGARS\*

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### INTRODUCTORY

In recent years advances in analysis of reducing sugars have consisted mainly of improvements in volumetric processes. While these methods are of the most general service, the older gravimetric methods still serve a useful purpose, particularly when only an occasional analysis is required or the sample is seriously contaminated or discolored.

The gravimetric methods have the disadvantage of being more time-consuming than the volumetric processes, but when modified by the introduction of volumetric methods for the determination of the reduced copper they approach the volumetric methods in respect of convenience and rapidity.

Four methods for the determination of reduced copper will be discussed in the present report, namely, direct weighing of cuprous oxide, titration with thiosulfate, and titration by the oxidizing reagents potassium permanganate and potassium dichromate.

### I. DIRECT WEIGHING OF CUPROUS OXIDE

The method of estimating reduced copper by direct weighing of cuprous oxide was employed by Munson and Walker<sup>1</sup> for determining the fundamental copper-sugar equivalents in their table. The greatest difficulty in

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<sup>1</sup> *J. Am. Chem. Soc.*, **28**, 666 (1906).

this procedure arises from the fact that filtration of a boiling solution of caustic alkali is a very severe treatment of the asbestos mat in the Gooch crucibles. Munson and Walker met this by prescribing a thorough preparation of the asbestos by digestion for many days with acid and with alkali alternately. The temptation is strong to curtail this preliminary treatment of the asbestos.

Recently Brewster and Phelps<sup>1</sup> described a method for the treatment of asbestos for filtration of sugar solutions preparatory to a color analysis. These authors prescribe boiling for 30 minutes 25 grams of asbestos with 250 cc. of 25 per cent sodium hydroxide followed by washing with boiling water. The asbestos, from which most of the water has been pressed, is then digested with 250 cc. of concentrated hydrochloric acid and 25 cc. of concentrated nitric acid on a steam bath for 30 minutes. It is again washed with boiling water. This operation can be completed in about 2 hours in contrast to the long period of digestion prescribed by Munson and Walker.

In the present investigation the method of Brewster and Phelps was used. For preparation of the crucibles a fairly thick mat was required, as the treatment removed in great part the finer particles of asbestos. In some instances a large volume of waste Soxhlet reagent was filtered through the crucibles with the highest vacuum attainable by the aspirator. The crucibles were dried, weighed, and subjected to a critical test. A volume of about 100 cc. of boiling Soxhlet Reagent No. 2 was poured through the crucibles with the vacuum regulated to complete the filtration in about 40 seconds, thereby simulating the conditions of the sugar analysis except for the presence of copper and sugar. When the crucibles were redried and reweighed, most of them maintained the same weight, while a few lost about 0.1 mg. No crucible lost as much as 0.2 mg.

Following Munson and Walker's procedure in detail the writer made one series of 11 determinations of cuprous oxide precipitated by 117 mg. of dextrose. The mean weight found, namely, 258.7 mg., agreed with Munson and Walker's tabulated value within 0.1 mg. The average deviation of a single experiment from the mean value was 0.4 mg.

After the weight of cuprous oxide had been determined the precipitate was dissolved in nitric acid and subsequently titrated with standard thiosulfate.

The mean of twelve titrations of total copper by the thiosulfate method agreed within 0.1 mg. with Munson and Walker's tabulated value. The ratio of copper to cuprous oxide, both determined independently, proved to be 0.8883, while stoichiometric theory requires a ratio of 0.8882, an agreement fortuitously exact. The agreement corroborates Munson and Walker's statement that cuprous oxide has a sufficiently exact composition to justify its conversion to copper by a numerical factor. This being

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<sup>1</sup> *Ind. Eng. Chem., Anal. Ed.*, 2, 373 (1930).

true, no useful purpose is served by converting cuprous oxide to copper (or cupric oxide) by chemical methods. Indeed such a procedure serves only to increase the hazard of an alteration of weight of the asbestos mat. The practice of weighing cuprous oxide is correct only if the sample consists of pure sugars. If the precipitated copper is contaminated neither reduction to copper nor ignition to cupric oxide will with certainty yield an uncontaminated precipitate.

In view of these considerations, the writer, as Associate Referee on Chemical Methods for Reducing Sugars, recommended that paragraph 44, page 381, *Methods of Analysis*, A.O.A.C., 1930, which describes the reduction of cuprous oxide in hydrogen, be discarded.

The method of weighing cuprous oxide was found to be so tedious and so subject to the possibility of an altered weight of the asbestos mat unless laborious precautions were taken, that all subsequent determinations of total copper were made by thiosulfate titration.

## II. THIOSULFATE METHOD

The thiosulfate titration was carried out essentially as described in the official methods.<sup>1</sup> The treatment with bromine to oxidize the oxides of nitrogen was avoided by allowing the solutions to evaporate on the steam bath to approximate dryness. If basic copper nitrate separated it was dissolved by addition of a few drops of dilute sulfuric acid. The solutions, made alkaline and acidified with a slight excess of acetic acid, were then diluted to such a volume (previously marked on the Erlenmeyer flask into which the copper nitrate was filtered) that the addition of the potassium iodide and thiosulfate would make the final concentration of potassium iodide 4 grams in 100 cc. The solution of KI, made up in a concentration of 4 grams in 10 cc., was added very slowly from a buret and mixed by constant agitation. Just the quantity required for the titration was made up each day.

The thiosulfate was standardized against very pure copper four times during the series of experiments. The total change in normality was about one part in a thousand.

## III. PERMANGANATE METHOD

A very old method for the determination of cuprous oxide is one in which the precipitate is dissolved in an acidified ferric sulfate solution and the resulting ferrous sulfate determined by titration with standard permanganate. It is known that if the permanganate is standardized by iron or sodium oxalate the analytical results are too low. The recommended procedure<sup>1</sup> is to standardize the solution by titrating the copper reduced by a given concentration of sugar and in separate analyses determine the true copper by electrolysis. In order to diminish the acci-

<sup>1</sup> *Methods of Analysis*, A.O.A.C., 1930, 380.

dental errors of sugar analysis a number of determinations must be made. Because permanganate is subject to change, the standardization must be repeated at relatively frequent intervals of time. This procedure is obviously laborious and unsatisfactory.

The writer suggests the possibility that under a standard procedure the permanganate method, in which the permanganate is standardized against sodium oxalate,<sup>1</sup> may yield reproducible results for reduced copper that may not agree with the true total copper, but that when used in conjunction with a tabulated series of empirical "apparent" copper-sugar equivalents may be equally serviceable. In this paper such an empirical series is presented.

The permanganate was made up with an initial normality of 0.15519, as standardized against pure sodium oxalate. It was filtered through dry asbestos and standardized five times during the course of the measurements, suffering a total loss of 0.2 per cent. The copper value of the solution was found by dividing ten times the determined normality by 0.15731 the latter figure being the normality of a solution, 1 cc. of which is equivalent to 10 mg. of copper.

The ferric sulfate solution was made up by dissolving 40 grams of crystals (which usually contain about 9 molecules of water of crystallization) in water containing 50 cc. of concentrated sulfuric acid, and allowing the mixture to remain on the steam bath until the salt was dissolved. Permanganate was added dropwise until a barely perceptible color of the permanganate ion remained. It was then cooled, made to 1 liter, and filtered.

In carrying out the analytical procedure the asbestos mat with the precipitate of cuprous oxide was transferred back to the reaction beaker and disintegrated with the addition of hot water. Fifty cc. of hot ferric sulfate solution was poured through the crucible into the beaker. The titration was immediately started without awaiting complete solution of the precipitate. Permanganate was run in until the approach of the end point became apparent. The asbestos was then examined by holding the beaker above the level of the eye. It always contained undissolved particles of cuprous oxide which were laboriously brought into solution by tapping each particle with a glass rod. When solution was complete the titration was continued to the change of color from bright green to gray. The slight excess of permanganate was estimated by adding full drops of a ferrous sulfate solution of about one-fifth the normality of the permanganate to a reappearance of the green.

Ferric sulfate solutions, particularly after long exposure to light, usually have an appreciable reducing power in the presence of permanganate. It was necessary, therefore, to determine a blank by adding perman-

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<sup>1</sup> McBride, *J. Am. Chem. Soc.*, 34, 393 (1912).

ganate dropwise to 50 cc. of the hot solution and titrating back with ferrous sulfate.

After an extended study of this method the writer finds but little to recommend it. In addition to the inherent defects of permanganate as a volumetric reagent, namely, its relative instability and the opaqueness of its solutions, the cuprous oxide dissolves with exasperating sluggishness. Moreover, there is always an unknown oxidation of the ferrous sulfate by air before and during the titration. While ferrous sulfate alone is but slowly oxidized by air, it is far more rapidly oxidized in the presence of copper sulfate. This oxidation by air is probably one of the reasons for the low results obtained by the permanganate method.

An effort was made to follow the procedure of Bisson and Sewall,<sup>1</sup> who added permanganate in excess to the precipitate before acidification with sulfuric acid. In no case could the precipitate be made to dissolve without imposing conditions which would decompose the permanganate and vitiate the results.

#### IV. ELECTROMETRIC DICHROMATE METHOD

In a previous report Jackson and Mathews<sup>2</sup> described a method for the determination of cuprous oxide in which standard potassium dichromate in excess was used to oxidize the cuprous oxide in hydrochloric acid solution and the excess of oxidizing agent was determined by a back titration with ferrous sulfate to an electrometric end point. The details of operation are described in the cited reference.

#### EXPERIMENTAL RESULTS

By the methods which have been outlined a comprehensive series of measurements was made of the reducing power of pure dextrose at ten concentrations ranging from 20 to 227 mg. At each concentration of sugar at least four analyses of the precipitated copper were made by titration against each of the three standard reagents, thiosulfate, dichromate, and permanganate.

The dextrose, a Bureau of Standards Standard Sample, was prepared by crystallization from aqueous solution in the anhydrous crystalline form. The sample suffered no loss in weight when subjected to a temperature of 105°C. for two hours. For the twelve or more analyses at each concentration of sugar, 1 liter of solution was prepared of such sugar content that a calibrated 50 cc. pipet delivered the selected weight of dextrose.

The alkaline tartrate constituent of the Soxhlet reagent was made with sodium hydroxide freed from carbonate by filtration of a 50 per cent solution through asbestos. The alkali content of the filtrate was determined by titration of weighed samples.

<sup>1</sup> *This Journal*, 10, 120 (1927).

<sup>2</sup> *Ibid.*, 15, 199 (1932).



TABLE 1.—*Reduction experiments with dextrose by the Munson-Walker method*  
(All data are expressed in milligrams.)

1	2	3	4	5	6	7	8	9	10	11	12	13	14	15
ORDER OF EXPERIMENT	WEIGHT OF DEXTROSE TAKEN	COPPER FROM MUNSON AND WALKER'S TABLE	COPPER BY THIOSULFATE				COPPER BY DICHROMATE				COPPER BY PERMANGANATE			
			FOUND	CALCULATED <sup>1</sup>	FOUND MINUS CALCULATED	FOUND MINUS MUNSON AND WALKER'S VALUE	FOUND	CALCULATED <sup>2</sup>	FOUND MINUS CALCULATED	FOUND MINUS COPPER BY THIOSULFATE	FOUND	CALCULATED <sup>3</sup>	FOUND MINUS CALCULATED	FOUND MINUS COPPER BY THIOSULFATE
5	20	41.7	41.7	41.2	+0.5	0	40.7	41.0	-0.3	-1.0	40.2	40.5	-0.3	-1.5
7	43	88.1	87.3	87.6	-.3	+0.8	87.3	87.2	+1.1	0	85.4	86.2	-.8	-1.9
3	66	133.4	133.1	133.0	+1.1	-.3	132.4	132.3	+1.1	-0.7	130.5	130.8	-.3	-2.6
8	89	177.7	177.1	177.3	-.2	-.6	176.2	176.4	-.2	-.9	174.2	174.5	-.3	-2.9
1	117	229.9	229.8	229.8	0	-.1	228.6	228.7	-.1	-1.2	259.0	259.0	0	-3.6
10	135	262.5	262.6	262.8	-.2	+1.1	261.4	261.5	-.1	-1.2	300.7	299.8	+9	-3.7
4	158	303.3	304.4	304.0	+4	+1.2	303.0	302.6	+4	-1.4	339.9	339.5	+4	-4.2
6	181	342.9	344.1	344.1	0	+1.2	342.1	342.5	-.4	-2.0	378.8	378.3	+5	-4.5
2	204	381.4	383.3	383.2	+1	+1.9	382.1	381.4	+7	-1.2	415.2	406.1	-.9	-5.8
9	227	418.7	421.0	421.2	-.2	+2.3	418.9	419.3	-.4	-2.1				

<sup>1</sup> Formula (1), p. 300.

<sup>2</sup> Formula (2), p. 300.

<sup>3</sup> Formula (3), p. 300.

TABLE 2.—*Precision of analysis*  
(Figures show the number of analyses that deviated from the calculated value by the per cent indicated in the column heading.)

DEX- TROSE	TETRASULFATE												DICHROMATE												PERMANGANATE														
	PER CENT ERROR		0	.1	.2	.3	.4	.5	.6	.7	.8	.9	>1.0	PER CENT ERROR		0	.1	.2	.3	.4	.5	.6	.7	.8	.9	>1.0	PER CENT ERROR		0	.1	.2	.3	.4	.5	.6	.7	.8	.9	>1.0
	COPPER													COPPER													COPPER												
mg. 20	41.2												3	41.0			1								2	40.5						1	1						2
43	87.6													87.2	1	1		1	1							86.2								1	1	1	1		
66	133.0	1	1	2										132.3		1	3	1								130.8	1	1	1			2				1			
89	177.1		3	1										176.4		2	2	3	1	1	1					174.5		1	1	1			1	1	1				
117	229.8			2	2									228.7	2	3	2	3	1																				
135	262.8	2	2											261.5		2	2									259.0	2				1	1							
158	304.0	1	3											302.6	1	2	1									299.8		1	2			1							
181	344.1	4												342.5	1	1	3									339.5	1			2		1							
204	383.2	4	2											381.4		2	1		1							378.3	1	2	1			1							
227	421.2	2	2											419.3	2	1	1									416.1	1	1		1		1							
Total		14	12	8	3							3			7	16	12	11	3	2	1	1		2			6	6	2	8	4	5	2		2	1		3	

Much emphasis has been placed upon the necessity of regulating the flame under the reaction beaker to bring the mixture to the boiling point in 4 minutes. Of equal importance, but less subject to control, is the total time required to complete the filtration after the 2-minute period of boiling, for during this time the reaction mixture is approximately at boiling temperature and any great variation results in a change of the effective time of reduction.

In one series of experiments in which 220.5 mg. of copper was precipitated in 2 minutes, the amount of precipitate increased at the rate of about 3 mg. a minute. Unless the time required for filtration is fairly uniform appreciable variations in the results will occur. In the present experiments the rate of filtration was roughly controlled by adjusting the vacuum to give a total time of filtration of 40–50 seconds.

Blank determinations of the autoreduction of the Soxhlet reagents used in the present experiments were made by boiling the mixture in the usual manner without the addition of sugar. After the filtration the asbestos was moistened with a few drops of nitric acid and the solution was washed into a beaker and evaporated to dryness. The residue was dissolved in dilute acetic acid, transferred to a test tube, and made to a volume of about 5 cc. A drop of dilute ferrocyanide was then added. The sample was compared colorimetrically with a series of standards containing 0.1, 0.2, and 0.3 mg. of copper, respectively. All blank tests showed the presence of copper qualitatively, but only in one instance was as much as 0.1 mg. precipitated. No correction for autoreduction was applied to the measurements which are tabulated.

The experimental data are assembled in Table 1. Each analytical result is the mean of at least four determinations. In order to detect progressive systematic errors the order of experiment was made unsystematic (see Column 1). The copper found in each series of ten concentrations of sugar was related to the dextrose taken by the method of least squares. This computation yielded the respective formulas:

$$\text{Cu (by thiosulfate)} = 2.0800 d - 0.000989 d^2 \quad (1)$$

$$\text{Cu (by dichromate)} = 2.0696 d - 0.000980 d^2 \quad (2)$$

$$\text{Cu (by permanganate)} = 2.0435 d - 0.000926 d^2 \quad (3)$$

in which the copper and dextrose ( $d$ ) are expressed in milligrams.

The weights of copper calculated by these formulas are shown in Columns 5, 9, and 13, respectively, and the deviation of experimental from calculated values in the respective adjacent columns.

In Column 7 are given the deviations of the total copper determined by thiosulfate titration from the values tabulated by Munson and Walker. While the agreement is fairly satisfactory in concentrations up to 135 mg., the deviations above this concentration increase progressively to more than one-half per cent in the final value. The lack of agreement in these higher concentrations suggests the need of further study because

this is the portion of the table where the method is at its best and is capable of yielding results of the highest precision. The discrepancies revealed by these analyses will receive further attention.

The electrometric dichromate method for reduced copper is somewhat less exact than the thiosulfate titration, as is shown by the larger residuals in Column 10 compared with those in Column 6. The deviations of the observed from the calculated values, however, do not greatly exceed one part in a thousand, a degree of precision satisfactory for usual purposes. The striking feature, shown in Column 11, is that with the exception of the first two determinations the values for copper are uniformly almost exactly one-half per cent lower than the values for total copper by thiosulfate. This suggests that the cuprous oxide is oxidized by air to the extent of one-half per cent between the time of its filtration and the addition of the standard dichromate or that cuprous oxide carries down by occlusion some cupric copper, or conceivably that a small amount of a copper oxide intermediate between cupric and cuprous oxides is formed. In any of these events the ratio of copper to cuprous oxide by weight is affected by only five parts in ten thousand, but any oxidation process shows the discrepancy at its full value.

The dichromate titration is by far the most convenient and most expeditious of all methods for cuprous oxide and since its precision is but slightly less than that of the thiosulfate method it is deemed worthy of further study. The values for the reduced copper are slightly different from those for total copper, but once the copper-sugar equivalents are established they are equally serviceable.

The permanganate method yields the least reproducible results of all those investigated. The mean residual (Column 14) is 0.49 mg., which is to be compared with 0.28 (Column 10) for the dichromate method and 0.20 (Column 6) for the thiosulfate method. The values for copper are from 1 to 2 per cent lower than those found by the thiosulfate method which suggests that in addition to the effect which was discussed in connection with the dichromate titration there occurred an oxidation of the ferrous sulfate before the addition of permanganate. The method is so cumbersome and susceptible to insidious sources of error that it is to be hoped that other oxidation methods can be found to displace it.

The data of the individual experiments, which are summarized in Table 1, are too voluminous to present in full, but the relative precision of analysis is shown strikingly in Table 2. The analyses in the columns headed zero error showed deviations of less than 0.05 per cent from the calculated values. The diagram shows the probable precision which can be expected in individual analyses, and also the greater precision which can be attained with higher than with lower concentrations of sugar.

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## BENZOYL PEROXIDE IN FLOUR—DETECTION AS BENZOIC ACID

By DOROTHY B. SCOTT (U. S. Food and Drug Administration,  
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Benzoyl peroxide is used extensively for bleaching flour. Of all the chemical agents used for this purpose, it is perhaps of the greatest interest to the analyst owing to the fact that although it is readily detected in freshly milled flour, it is difficult to detect after the flour is aged even a day or two. Jorgensen,<sup>1</sup> who made a complete study of bleached flour, states in effect that the analyst can be reasonably sure when a flour is bleached, but he cannot always detect the agent or the quantity of it used.

Benzoyl peroxide is used in the United States and Europe under various trade names, as for example Lucidol, Novadel, Novadelox, and Novadelox-B. These commercial preparations are mixtures of benzoyl peroxide and some relatively inert material. Jorgensen states that in Europe one part of benzoyl peroxide is mixed with five parts of acid calcium phosphate for use in flour, but in the United States the product called Novadelox analyzes about one part of benzoyl peroxide to four parts of acid calcium phosphate. No definite information was obtained in regard to the proportions of this product used in the actual bleaching of flour. It is used in the United States in conjunction with other bleaching agents, and the amount is presumably less than the proportion of 13 grams to 100 kg. of flour given by Jorgensen. The American distributors of Novadelox recommend that one pound be used to treat from 30 to 50 barrels of flour. On this basis the quantity of benzoic acid remaining in the flour would be 20–34 parts per million.

Considerable study has been given by the writer to the development of a suitable method for the detection of benzoyl peroxide. Previous work on flour freshly bleached shows that it can be detected by its oxidizing reaction, but after a few days' contact it is unlikely that this reaction can be obtained.

Monier Williams,<sup>2</sup> describes briefly results of work on this subject, and Illing<sup>3</sup> reports some modifications which he believes improve the Mohler test for benzoic acid. Leather<sup>4</sup> describes a new method for the detection of benzoic acid, and applies it to flour, but it is not clear whether he adds small quantities of benzoic acid to flour or uses commercially bleached flour. However, attempts by the writer to use Leather's method on flour known to have been bleached with benzoyl peroxide were unsuccessful so far as a positive test for benzoic acid is concerned. The method of Nicholls<sup>5</sup> was published after the method presented had been developed.

<sup>1</sup> Den Analytiske Paavising Af Blegning Af Hvedemel. Copenhagen (1928).

<sup>2</sup> British Report on Public Health and Medical Subjects No. 39 (1927).

<sup>3</sup> *Analyst*, 56, 224 (1932).

<sup>4</sup> *Ibid.*, 56, 299 (1931).

<sup>5</sup> *Ibid.*, 58, 4 (1933).

Using the delicate Mohler test as modified by Illing and a specially devised method of extraction and distillation, the writer obtained positive tests for benzoic acid on a large number of commercial samples of flour bleached with benzoyl peroxide.

The apparatus used in the determination of the Polenske number of fats and oils, or a similar apparatus, should be used in the distillation.<sup>1</sup> The method follows:

#### METHOD

To 500 grams of the flour in a 2 liter flask add 800 cc. of alcohol (95 per cent) and 5 cc. of sulfuric acid (1+1). Allow the mixture to stand for one hour, shaking the flask every few minutes, then transfer to a large Büchner funnel (inside diameter 186 mm., inside depth 75 mm.) and filter off the alcoholic extract. Rinse out the flask with 200 cc. more of the alcohol. Pour this mixture on the flour in the funnel and allow to stand without suction for one-half hour, then drain. Repeat, using 200 cc. more of alcohol. Pour the combined alcohol extracts into a large casserole, add 4 cc. of a 50% sodium hydroxide solution, mix thoroughly, and evaporate to dryness on the steam bath or hot plate.

Add 100 cc. of water to the casserole, mix thoroughly, and pour the mixture into the distillation flask, rinsing the casserole with 50 cc. of water. Neutralize with the sulfuric acid (1+1), and add 5 drops in excess, 50 grams of sodium chloride and about 5 grams of powdered pumice.

Connect the apparatus and distil the mixture briskly until a volume of 50 cc. remains. Regulate the flame to avoid boiling over, especially at the initial boiling point, and avoid any scorching at the end (an interfering color will develop if the alcoholic extract is scorched). Collect the distillate in a 250 cc. casserole to which has been added 1.5 cc. of approximately normal sodium hydroxide. Rinse the condenser with a small quantity of alcohol. Evaporate the distillate to about 15 cc. Decolorize by adding 100 cc. of a reagent made by combining and mixing thoroughly a solution of 45 grams of stannous chloride in 200 cc. of water with a solution of 7.5 grams of aluminum potassium sulfate in 300 cc. of water. Then add 5 cc. of the 50 per cent sodium hydroxide solution and 10 grams of calcium carbonate. Stir the mixture thoroughly, rinse into a centrifuge bottle with 25 cc. of water, centrifuge, and filter into a casserole. Make slightly alkaline to litmus paper and evaporate to 5 cc. Filter. If almost colorless, add 100 cc. of water, 10 drops of the sulfuric acid (1+1), 40 grams of sodium chloride, and about 5 grams of powdered pumice. Distil nearly to dryness and collect the distillate in 1.5 cc. of normal sodium hydroxide. Evaporate the distillate to 3 cc. If the filtrate is colored yellow repeat the decolorization before distilling. The second removal of color will rarely be necessary with wheat flour, but it may be necessary with rye flour.

When the evaporated distillate is practically colorless, pour into a test tube (15×125 mm.), rinsing out the casserole with a few drops of water. Heat in a beaker of boiling brine until the liquid is completely driven off and all drops of condensation water have disappeared. Cool, and add 0.1 gram of potassium nitrate and 1 cc. of concentrated sulfuric acid. Heat in boiling water for 20 minutes. Cool, add 2 cc. of water. Holding the tube under cold running water, add carefully 10 cc. of ammonium hydroxide (1+1). After mixing, add 2 cc. of 2% hydroxylamine hydrochloride solution and again mix thoroughly; place in a beaker of water kept at 65°C. for 5-6 minutes, cool, and filter. If benzoic acid is present, a reddish color

<sup>1</sup> *Methods of Analysis*, A. O. A. C., 1930, 322.

develops. It may best be observed by looking down through the test tube when the latter is placed over a white surface. Run a blank on reagents used.

*The following precautions must be observed:*

(1) Test the solution before distilling to be sure it is acid, and test the distillate before evaporating to be sure it is alkaline; (2) have the sodium benzoate absolutely dry before nitration (if there is any doubt on this point dry the test tube further in a vacuum oven at 100° C.); (3) after the nitration has proceeded for a few minutes, take the tube from the water and allow the sulfuric acid to run over its surface and come in contact with any solids deposited on the upper parts of the tube.

The method presented is not quantitative. From a series of experiments, the recovery was found to be about 25 per cent. As the Mohler test is very delicate, less than a milligram being easily detected, three alcohol extractions of the flour are satisfactory for a qualitative test.

The presence of benzoic acid in flour bleached with benzoyl peroxide was confirmed by the microchemical tests made by Leather and by Behrens-Kley.<sup>1</sup>

The thanks of the writer are extended to Joseph Callaway, Jr., Chief of the New York Station, U. S. Food and Drug Administration, and to C. F. Jablonski, W. E. Kirby, and J. S. Ard for their helpful suggestions in developing the method.

### VITAMIN A VALUE OF ALFALFA CUT AT DIFFERENT STAGES OF MATURITY\*

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The vitamin A value of alfalfa hay varies greatly with the conditions of the curing process. Russel<sup>1</sup> and Russel, Taylor and Chichester<sup>2</sup> found that alfalfa leaves that were dried by mechanical driers contain many times more vitamin A than leaves from field-cured alfalfa hay. Hauge and Aitkenhead<sup>3</sup> found that the vitamin A value of alfalfa is preserved either by treatment with heat during the drying process (mechanical driers) or by sterilization by autoclaving before drying, while the field-curing process is more or less destructive to the vitamin A value. Hartman<sup>4</sup> and Smith and Briggs<sup>5</sup> showed the variation of vitamin A in hays as affected by field-curing conditions. Furthermore, the high vitamin A value of butter produced by cows fed artificially dried grass, as compared with the butter produced by cows when fed field-cured grass, indirectly confirms these results as shown by Gillian, Heilbron, Morton, Bishop and Drummond.<sup>6</sup>

<sup>1</sup> *Organische Mikrochemische Analyse* (1922).

\* Published with the approval of the Director of the Purdue University Agricultural Experiment Station, Lafayette.

<sup>1</sup> *J. Biol. Chem.*, **85**, 289 (1929).

<sup>2</sup> *Proc. Exper. Biol. Med.*, **39**, 376 (1933).

<sup>3</sup> *J. Biol. Chem.*, **93**, 657 (1931).

<sup>4</sup> *Ibid.*, **92**, p. vii (1932).

<sup>5</sup> *J. Agr. Research*, **46**, 229 (1933).

<sup>6</sup> *Biochem. J.*, **27**, 878 (1933).

As the experiments of Hauge and Aitkenhead mentioned previously indicated that the vitamin A value of alfalfa may vary with its degree of maturity it seemed desirable to make a further study of the vitamin A value of alfalfa cut at different stages of maturity, and also to determine the effect of the various methods of curing on the preservation of the vitamin A value of the entire hay, of the leaves, and of the stems.

#### EXPERIMENTAL

The samples used were prepared from alfalfa selected at two stages of maturity. The first group of samples was prepared from luxuriant young alfalfa plants, cut when they were 10–12 inches high and before they showed any bloom. The second group of samples was prepared from vigorously growing alfalfa plants in the full-bloom stage. The samples comprising classes A, B and C of each group were cut from the same field on the same day, when the weather conditions were favorable for rapid field curing. Immediately after the hay had been cut, representative samples were removed to the laboratory for special treatments. Twenty samples were prepared and classified according to the curing processes used.

*Class A.*—One sample each of entire hay, of leaves, and of stems was prepared from alfalfa of each stage of maturity, a total of six samples. These were treated in an autoclave in the presence of live steam at a pressure of 17 pounds for 1 hour to destroy the enzymes, then placed on screens and dried by direct exposure to the sun.

*Class B.*—One sample each of entire hay, of leaves, and of stems was prepared from alfalfa of each stage of maturity. Without preliminary treatment, these samples were placed on screens and dried by direct exposure to the sun.

*Class C.*—One sample each of entire hay, of leaves, and of stems was prepared from alfalfa of each stage of maturity by field curing.

*Class D.*—One sample of hay was obtained from the same field of mature alfalfa as the above samples, but it had received a light rain during the field-curing process.

*Class L.*—One sample of western-cured alfalfa leaf meal that was submitted by a commercial company.

The vitamin A values of these samples of alfalfa were determined by biological assays and the use of the curative method. The number of rats employed for each dosage ranged from four to eight, and the sex distribution was about equal. Each animal was kept in an individual cage of a type that prevented access to excreta. The vitamin A deficient ration was given *ad libitum* in modified McCollum type feeding cups. The composition of the ration was as follows: casein (extracted), 18 per cent; ground white corn, 25 per cent; dextrin, 36 per cent; lard, 10 per cent; salt mixture No. 185 (McCollum and Simmonds<sup>1</sup>), 4 per cent; agar, 2 per cent; and yeast (irradiated), 5 per cent. During the preliminary depletion period, the rats were restricted to this ration until they showed definite symptoms of vitamin A deficiency. At this point, usually 2 to 3 weeks, the animals were given daily their respective test dose of alfalfa.

<sup>1</sup> *J. Biol. Chem.*, 33, 55 (1918).



In order to increase the accuracy of weighing the necessary quantities for each test dose and also to assure consumption of the less palatable materials, the alfalfa samples were diluted with the basal ration so that each preparation contained either 10 or 20 per cent of the sample to be tested. The test doses were placed in small glass dishes and fed to the rats individually. The results of the biological assays are reported in Sherman and Munsell<sup>1</sup> vitamin A units. The results are given in Chart 1.

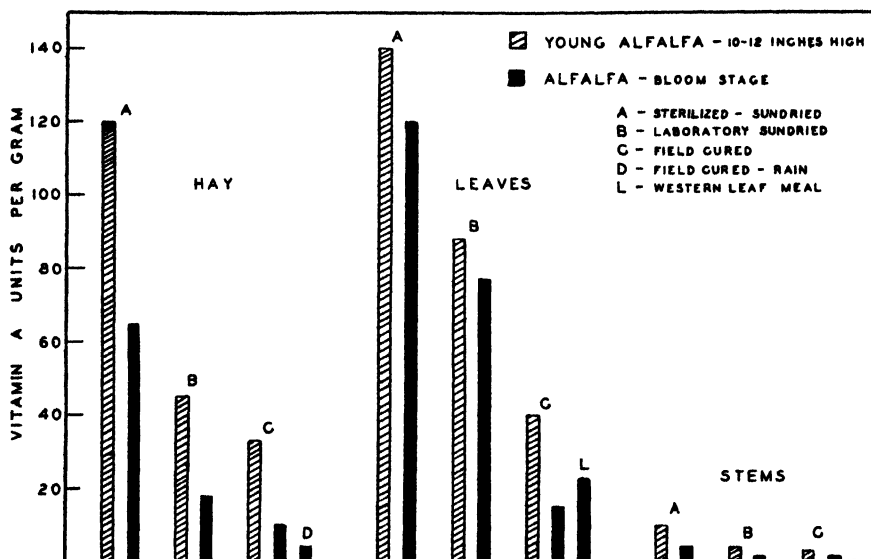


CHART 1.—SHOWING THE VITAMIN A VALUE OF ALFALFA FROM TWO STAGES OF MATURITY.

### DISCUSSION

The results of these experiments show that the vitamin A value of young alfalfa is much greater than that of alfalfa in the full-bloom stage. This relationship is consistent in all the tests on the various products prepared by the different methods of curing.

The difference in the vitamin A values of the samples produced by the various curing methods indicates the relative effectiveness of the various processes in preserving the vitamin A value of the alfalfa from the two stages of maturity. Sterilization, which destroys the enzymes, before drying, tends to preserve the vitamin A potency most effectively, giving products of high value. The relatively rapid drying of the alfalfa on screens (Class B) gives fairly good results. However, with the field-curing method (Class C), there is considerable loss of the vitamin A value. This confirms the earlier results of Hauge and Aitkenhead. The slight rain that fell on the more mature hay (Class D) during the field-curing process,

<sup>1</sup> *J. Am. Chem. Soc.*, 47, 1639 (1925).

caused a great deterioration in its vitamin A activity. It is possible to secure hay of higher vitamin A value from alfalfa in the bloom stage by efficient curing methods (mechanical driers) than from the younger plants cured under unfavorable field conditions.

These experiments also show that the vitamin A activity of the alfalfa is located chiefly in the leaves and that the stems are of low vitamin A value. Alfalfa leaves cured by effective methods were of high vitamin A value. In comparing Sample L, which was a western-cured leaf meal, with the other samples of leaves cured by the various processes, it is seen that it is markedly inferior to the samples that were sterilized immediately after cutting, although it is somewhat better than the field-cured leaves from the mature plants.

Analysis of these samples showed that the average protein content of the hay from the young alfalfa was 25.2 per cent while that from the older plants was 16.6 per cent. There was 30.8 per cent protein in the dried leaves from the young plants and 26.5 per cent protein in the leaves of the older plants. The stems from the young plants contained 17.9 per cent protein, and those from the older plants contained 10.7 per cent. Sterilization and other methods of curing did not affect the protein content of the samples. During the growth of the plant, the proportion of stems to leaves gradually increases, and at the same time there is an increase of cellulose. This tends to lower the protein and vitamin A value of the hay, as the richest source of both these nutritive factors is in the leaves. If care is not exercised, the feeding value of the hay may be further reduced by loss of leaves during the making of the hay. Thus it is apparent that the feeding value of alfalfa hay will depend upon the method of curing, the maturity of plants, and the retention of leaves.

#### SUMMARY

1. The vitamin A value of young alfalfa (10-12 inches high) is much greater than that of alfalfa in the bloom stage.
  2. The vitamin A potency of alfalfa is located chiefly in the leaves, and the stems are of low vitamin A value.
  3. Alfalfa products that were sterilized immediately after they had been cut, and then sun dried, had a much greater vitamin A value than unsterilized alfalfa either sun dried or field cured.
  4. Important factors affecting the vitamin A value of alfalfa hay are the degree of maturity of the plants, the conditions of the curing process, and the retention of leaves.
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## DETERMINATION OF NAPHTHALENE IN INSECTICIDES

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The methods presented give more accurate results than those obtained by procedures now used, and excepting the procedure for louse powders, they are also considerably shorter. The procedure for louse powders is recommended as a check method and for use when volatile compounds interfere with the volatilization method. The procedures given are adapted to every type of naphthalene insecticide now in use, and when necessary the analyst may modify them for new types as required.

## NAPHTHALENE IN MINERAL OILS (KEROSENE)

*Acetone-water mixture.*—Mix 90 cc. of acetone and 10 cc. of distilled water.

If cresols, phenols, or alkaloidal bases are present, extract them from a large sample, first with 10% sodium hydroxide solution, then with dilute acid, and finally with water.

Transfer a 10 cc. sample, free from the above substances, to a small separatory funnel, using a graduated pipet or a buret, and shake well with two portions of 20 cc. each of the acetone-water mixture. Allow each portion to separate well before draining. Obtain two 50 cc. Babcock cream bottles that balance each other within 3 grams and drain the two extracts into the heavier of the two bottles. Add 10 cc. of water to the combined extracts, shake, and let stand for 2 to 3 minutes. Pipet off the oil that rises to the top and return it to the separatory funnel. Extract the sample further with two additional 20 cc. portions of the acetone-water mixture, and transfer the extracts to the second Babcock bottle. Add 10 cc. of water to this bottle and shake. Balance the two bottles with a small quantity of the acetone-water mixture and centrifugalize both at about 1200 r.p.m. for 10 minutes. Pipet the top layers off carefully, using a steady suction. Drain both bottles into a 100 cc. volumetric flask and make up to the mark with acetone-water mixture. Pipet off a 50 cc. aliquot, transfer it with stirring into a 400 cc. beaker containing 250 cc. of saturated aqueous picric acid, allow to stand for at least 5 minutes with occasional stirring, and filter slowly with suction through a Gooch crucible with a removable bottom. The crucible should be fitted with a layer of filter paper covered with a fairly thick and well-packed layer of asbestos. The filtrate may be a little cloudy owing to a small amount of emulsified oil; if there is much cloudiness examine for solid particles. Wash the precipitate thoroughly with 0.2% solution of picric acid. Wash the beaker and remaining particles with the dilute picric acid solution and drain the beaker into the crucible for about one minute.

Transfer the contents of the crucible back into the beaker by pushing out the bottom and washing with hot, recently boiled, distilled water. Add 150–200 cc. of the hot distilled water and an excess of 0.1 *N* sodium hydroxide solution, and heat to boiling with constant stirring. Keep the solution near the boiling point and stir until all the naphthalene picrate particles are broken up. Continue the heating for about 5 minutes longer to insure complete reaction. Then allow the mixture to cool somewhat, add sufficient phenolphthalein to produce a deep red color, and titrate back to a yellow color with 0.1 *N* hydrochloric acid. From the number of cc. of sodium hydroxide required subtract 0.05 cc. for each 20 cc., and 0.05 cc. for the picric acid retained by the filter. The resulting number of cc. of 0.1 *N* sodium hydroxide times 0.012806 gives the weight of naphthalene in the sample.

**NAPHTHALENE IN LOW BOILING SOLVENTS**

Transfer an aliquot (containing not over 5 grams of naphthalene and not over 7 grams of para-dichlorobenzene) to a 100 cc. volumetric flask, using a graduated pipet or buret, dilute to the mark with chloroform, shake, and transfer a 10 cc. aliquot to a 200 cc. beaker containing 1 gram of picric acid and 10 cc. of chloroform. Stir, and evaporate off the solvent on the steam bath without violent boiling. When 1 to 2 cc. remains, remove the beaker from the bath and drive off the remainder of the solvent with a gentle current of air. Add immediately 15 cc. of alcohol and warm just enough to dissolve the mixture, then add 100 cc. of distilled water, stir, and allow the mixture to chill in a cold water bath. Filter, and titrate as stated in the procedure for naphthalene in kerosene. The filtrate should be clear unless much essential oil is present.

**NAPHTHALENE WITH WOOD CHIPS AND ESSENTIAL OIL**

• Weigh a sample containing not over 1 gram of naphthalene into a large paper extractor shell, pack the sample down and cut off the empty top of the shell. Place the shell in a cylindrical glass funnel just large enough to accommodate it, close the stopcock and pour 40 cc. of hot alcohol onto the sample. Stopper the funnel and allow to stand for 5 minutes. Then move the shell up and down in the solvent with a stirring rod. Tap the rod against the side of the funnel to remove adhering solvent from the rod. Stopper the funnel again and repeat the stirring two or three times during the next 5 minutes. Then drain the solvent as completely as possible into a 100 cc. volumetric flask. Repeat the extraction with another 40 cc. portion of hot alcohol. Extract a third time with 20–25 cc. depending on the bulk of the sample. Cool the volumetric flask containing the extracts and make up to volume with alcohol. Transfer a 50 cc. aliquot to a beaker containing 200 cc. of saturated aqueous picric acid solution, stir, and let stand for a few minutes in a cold water bath. Filter and titrate as stated in the procedure for naphthalene in kerosene. The filtrate may be quite cloudy if much oil is present in the sample. Large lumps of naphthalene picrate should be mashed with a stirring rod to aid the reaction with the sodium hydroxide solution.

**NAPHTHALENE IN MIXTURES WITH PARA-DICHLOROBENZENE, CAMPHOR, AND INORGANIC FILLERS**

Weigh out a sample containing approximately 1 gram of naphthalene, dissolve in concentrated acetic acid, and transfer to a suitable volumetric flask. Fill the flask to the mark with concentrated acetic acid. Mix in a 300 cc. beaker 80 cc. of water, 40 cc. of concentrated sulfuric acid, and sufficient acetic acid to give 70 cc. of acetic acid with the added aliquot. Then add an aliquot containing 0.10–0.15 gram of naphthalene, stir, and add 0.5 *N* potassium permanganate solution from a buret, keeping the temperature of the solution at about 70°C. When the rose color formed does not fade rapidly to orange, remove the buret and heat the solution rapidly to 91°. Keep the solution at 90–91°, and add more permanganate solution just fast enough to keep the solution at the point where the rose and orange colors merge. The color should not become a deep rose, and it should be allowed to fade to orange before each addition. As the end point approaches, add the solution dropwise until the rose color takes more than 5 to 6 seconds to fade to orange. Add one more drop of permanganate solution, and if the rose color persists for 6 seconds, take the reading at this point. Calculate the naphthalene, using the following equation:

$$\frac{\text{normality of KMnO}_4 \times 0.7115 \times \text{cc. KMnO}_4}{\text{weight of sample used}} = \text{percentage of naphthalene.}$$

(The analyst should acquaint himself with the above end point by titrating a known amount of naphthalene.)

## NAPHTHALENE IN LOUSE POWDERS AND SIMILAR MIXTURES

*Apparatus.*—The outlet from a steam generator provided with a safety tube is connected with a glass tube leading to the bottom of a 500 cc. Kjeldahl flask. An outlet from the top of the Kjeldahl flask should be made of 7 mm. glass tubing. The outlet should project only a few cm. into the Kjeldahl flask and it should be connected to the condenser with a cork stopper. The condenser is made of straight glass tubing of about 20 mm. diameter and long enough to reach nearly to the bottom of the receiver and to project about 1 foot above the receiver. The projecting part of the condenser is fitted with a water jacket. The receiver is a 1 liter Erlenmeyer flask with a stopper which is bored to accommodate the condenser and a small vent tube. When in use, the end of the condenser tube should be about 1 cm. above the bottom of the receiver, which contains enough distilled water to allow immersion. The receiver should be weighted and immersed in a water bath while in use.

*Procedure.*—Weigh a sample containing at least 2 grams of naphthalene, and transfer to the Kjeldahl flask. Add about 100 cc. of water and a small quantity of sodium hydroxide solution. Immerse the receiver in cold water, run a stream of water through the condenser jacket, and steam distil the sample slowly for 1 hour. When the distillation is complete, wash the naphthalene into the receiver with water, using a glass rod to loosen particles that adhere to the sides of the condenser. If necessary, the condenser may be heated or rinsed with hot water to aid in this step.

Acidify the distillate and rinsings in the receiver with dilute sulfuric acid, and filter with suction through a Büchner funnel fitted with a tight filter paper. Wash the naphthalene with a small amount of water, transfer the filter paper and naphthalene immediately to a suitable beaker, and rinse the remaining particles from the funnel with acetic acid. Dissolve the naphthalene in at least 50 cc. of acetic acid, warming if necessary to hasten solution. Filter the solution through a fast filter or glass wool and wash the filter thoroughly with acetic acid. Make up to volume in a suitable volumetric flask with acetic acid. Titrate an aliquot as stated in the procedure for naphthalene in para-dichlorobenzene mixtures.

## DISCUSSION

The first three methods are modifications of the picrate precipitation principle which has been used for some time in naphthalene determinations. Previous methods were not suitable, however, for the mixtures mentioned in this paper.

In the procedure for naphthalene in kerosene, the acetone-water mixture was found to be the best means of extracting the naphthalene without retaining mineral oils, which would cause errors in the filtration. Solid aromatic hydrocarbons do not occur naturally in kerosene in sufficient amounts to cause an appreciable error, nor does as much as 5 per cent of crude coal tar in the sample affect the results materially. The writer analyzed a sample of crude creosote after freezing out most of the solid hydrocarbons and the amount of picrate obtained was equivalent to 1.3 per cent naphthalene. A good part of this was due to naphthalene itself. Phenols and nicotine would give interfering picrates, but they are removed by acid and alkali washing.

Naphthalene is invariably lost when determined by evaporation from low-boiling solvents. The writer discovered that the naphthalene picrate

has a sufficient association in certain solvents to enable it to be recovered with very slight loss of naphthalene. Chloroform was found to be the most practical solvent for this use. Naphthalene picrate apparently dissociates in alcohol and certain other oxygenated solvents to such an extent that considerable naphthalene is lost on evaporation. Dry naphthalene picrate also decomposes considerably on exposure to air.

Before adopting the procedure for naphthalene in wood chips, attempts were made to extract the naphthalene by steam distillation. Varying results were probably due to incomplete extraction and the presence of distillation products of wood. Chloroform extraction and evaporation as picrate gave results about 0.3 per cent low, probably because of the loss during the evaporation of the large quantity of chloroform required for the extraction. After trying several types of extraction apparatus the writer found the one described to be the most satisfactory. Coal tar products and insoluble fatty acids may interfere in this method if present in appreciable quantities.

Para-dichlorobenzene, camphor, and essential oils do not interfere in the proposed picrate methods.

The methods for naphthalene with para-dichlorobenzene and in louse powders are based on the writer's discovery that naphthalene can be oxidized quantitatively to phthalic acid. It is known that naphthalene is oxidized by permanganate in acid solution to a mixture of phthalonic and phthalic acids. Although it is considered difficult to stop the oxidation of most organic compounds at an intermediate point, by careful control of conditions it is possible to accomplish this quantitatively with naphthalene as directed in this paper. The results obtained indicate that the optimum conditions have been obtained in regard to the nature of the oxidizing agent, the amount and concentration of acid, the solvent, and the temperature of the reaction. The reaction proceeds rapidly at first, but after the phthalonic acid stage is reached the reaction is slow and excess permanganate must be avoided or phthalic acid will be decomposed. The end point is not very sharp, but after the analyst becomes familiar with it he can obtain accurate results. The theoretical by-products of the reaction are formic and oxalic acids, but these are oxidized as fast as they are formed. Nine oxygens are consumed in the oxidation of one molecule of naphthalene to phthalic acid.

Para-dichlorobenzene is not oxidized by permanganate in the proposed methods. According to Beilstein,<sup>1</sup> camphor is easily oxidized by permanganate in alkaline solution, but difficultly so in neutral solution. Varying results obtained with these methods in the presence of large amounts of camphor indicate that the camphor itself is not oxidized but the camphor oil present as an impurity causes interference. As the amount of camphor in naphthalene mixtures is rarely large, the error caused by the camphor

<sup>1</sup> *Handbuch der Organischen Chemie*, 4th ed., VII, 104 (1925).

oil can be ignored in nearly all cases. One per cent of essential oil will give an error of 0.5–1.5 per cent in the direct titration. As the quantity of essential oil in moth cakes is usually very small, the error should be slight.

Calcott, English, and Downing<sup>1</sup> published a method for determining naphthalene by distillation, sulfonation, and oxidation by vanadic acid. The reaction is quantitative, but para-dichlorobenzene and camphor are also oxidized by the vanadic acid. The proposed methods are shorter and more practicable for insecticides.

### Experimental results

SAMPLE	COMPOSITION	DETERMINED			AVERAGE
Naphthalene in mineral oils					
1	5 grams per 100 cc. in kerosene	5.00	4.88	5.00	4.96
2	2 grams per 100 cc. in kerosene	1.92	2.22	2.15	2.10
3	2 grams per 100 cc. in kerosene with 10% of a mixture of oils of citronella, pine, cedar leaf, turpentine, and wintergreen	1.90	1.90	1.92	1.91
Naphthalene in low-boiling solvents					
4	2 grams per 100 cc. in a mixture of <i>p</i> -dichlorbenzene and carbon tetrachloride	1.95	1.92	2.05	1.99
5	15 grams per 100 cc. in a mixture of benzene and carbon tetrachloride	14.93	15.29	15.19	15.11
		15.22	14.93		
Naphthalene with wood chips and essential oil					
6	5% naphthalene, 20% cedar leaf oil, and 75% pine wood chips	5.05	4.85	4.74	4.96
7	16% naphthalene, 20% cedar wood oil, and 64% pine wood shavings	15.85	16.04		15.95
Naphthalene with <i>p</i> -dichlorbenzene and fillers					
8	commercial naphthalene	99.26	99.47	99.68	99.47
9	refined naphthalene	100.31	99.89	100.21	99.89
10	50/50 refined naphthalene and <i>p</i> -dichlorbenzene	49.74	49.95	49.74	49.95
		49.74	49.74	50.15	50.05
		49.95	49.84	49.74	49.84
11	16.29% refined naphthalene, and 83.71% <i>p</i> -dichlorbenzene	16.08	16.16	16.11	16.12
12	27.73% refined naphthalene, 54.80% <i>p</i> -dichlorbenzene, and 17.46% camphor	28.49	28.55		28.52
13	20% refined naphthalene, 40% <i>p</i> -dichlorbenzene, and 40% camphor	20.50	20.61	20.73	20.61

<sup>1</sup> *Ind. Eng. Chem.*, 16, 27 (1924).

14	50/50 refined naphthalene and sodium chloride	50.26	50.16	49.95	49.95	50.08
15	8% refined naphthalene in a mixture of tobacco powder and inorganic filler, with a small amount of crude carboic acid	7.93	7.96	7.96	8.01	7.97
16	5% naphthalene in a mixture of tobacco powder, sulfur, phenols, and inorganic filler	5.04	5.06	5.02	5.01	5.03
17	10% naphthalene in a mixture of tobacco powder, pyrethrum powder, sulfur, and Liquor Cresolis Compositus	9.99	9.97	10.03	9.97	9.99
18	A commercial sample containing naphthalene, sulfur, tobacco, and sodium fluoride, giving 7.35 and 7.50% by sublimation	7.65	7.68			7.67
19	A commercial sample containing naphthalene, tobacco powder, and sodium fluoride, giving 9.75% by sublimation	9.66	9.73			9.70
20	A commercial sample containing naphthalene, tobacco powder, sulfur, and about 1 per cent <i>p</i> -dichlorobenzene, giving 73.18% by sublimation and allowance for the <i>p</i> -dichlorobenzene	73.31	73.52			73.42

## CONCLUSIONS

The procedure for naphthalene in kerosene is shorter and more accurate than other methods. For example, one popular method that specified passing air through the kerosene and into picric acid solution took two or three days, and the results often varied one per cent or more from the amount of naphthalene present. The procedure for naphthalene in low-boiling solvents is rapid and much more accurate than distillation or direct evaporation from solvents. The procedure for naphthalene in wood chips shows some variation due to the difficulties of extraction, but the results are more accurate than those obtained by previous methods. The procedures for naphthalene with para-dichlorobenzene and in louse powders give excellent results when the analyst becomes familiar with the titration conditions. The presence of sufficient essential oil to interfere with titration is rare. The procedure for louse powders is recommended only as a check method and for use when volatile compounds interfere with the sublimation method.

The writer wishes to acknowledge the encouragement given by Joseph Callaway, Jr., of the U. S. Food and Drug Administration Station in New York.



DETECTION OF GELATIN IN CULTURED BUTTERMILK  
AND COTTAGE CHEESE

By G. A. RICHARDSON and N. P. TARASSUK (Division of Dairy Industry,  
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The Stokes method<sup>1</sup> for the detection of gelatin in milk and cream was accepted as official by the Association of Official Agricultural Chemists.<sup>2</sup> It has been recognized, however, that this method gives erroneous results in the case of sour milk, sour cream, cultured buttermilk and cottage cheese. This is presumably due to the presence in these products of substances resulting from the partial hydrolysis of the proteins, such substances resembling gelatin in their behavior to the reagents used in the Stokes test. The Seidenberg hot water modification<sup>3</sup> was designed to make the Stokes test specific for gelatin, but it often fails clearly to differentiate gelatin from the hydrolytic products of the proteins, especially in cultured buttermilk and cottage cheese. For example, Mendelsohn<sup>4</sup> reported that the modification failed in the case of cream to which rennet had been added, a positive test for gelatin being obtained on samples that were known not to contain gelatin.

Preliminary studies in connection with cultured buttermilk showed that the Seidenberg modification yields fairly accurate results under well-controlled conditions. The test, however, was found to be too uncertain, especially from the standpoint of regulatory laboratories. If certain discriminating observations are made, the method of Stokes leads to fairly correct decisions in the detection of gelatin in cultured buttermilks whether fresh or old, with or without rennet. Thus, when picric acid is added to the filtrate resulting from the addition of mercuric nitrate, old samples and those containing gelatin or rennet will become cloudy immediately. On shaking and standing, precipitates will form in all samples of cultured buttermilks, more especially in old samples and those to which rennet has been added. The types of precipitates are different. Those resulting from compounds derived from proteolysis are flocculent, settle rapidly, are non-adhesive to the walls of the container, and are easily disturbed. The serum is clear. The precipitates of gelatin-picric acid are more crystalline in nature, settle slowly, and adhere tenaciously to the bottom and sides of the container. The serum will remain opalescent for days. By making use of these observations during the past three years, three separate classes of upper division students were enabled to report correctly on heterogeneously arranged groups of unknown samples of cultured buttermilk.

It is imperative, however, that for precise work the method be as inde-

<sup>1</sup> *Analyst*, 22, 320 (1897).

<sup>2</sup> *Methods of Analysis*, A.O.A.C., 1930, 223.

<sup>3</sup> *Ind. Eng. Chem.*, 5, 927 (1913).

<sup>4</sup> *Analyst*, 55, 567 (1930).

pendent as possible from a procedure in which a comparison of types of precipitate is used in drawing final conclusions. In addition, the method should also be applicable to cottage cheese, with and without rennet. The procedure outlined above does not yield satisfactory results with cottage cheese.

Jacobs and Jaffe<sup>1</sup> recently reviewed the literature on the detection of gelatin in dairy products and reported a new method. They use basic lead nitrate as the protein precipitant, and calcined charcoal as adsorbent for the "pseudo-gelatins" formed in the souring process. Picric acid or tannic acid is used as the final precipitant. This method, however, in the hands of the writers gave erroneous results with very old samples of cottage cheese and cultured buttermilk, and with those containing rennet.

The successful use of trichloroacetic acid, especially in high concentrations, for the precipitation of the proteins of milk suggested that this acid might aid in differentiating gelatin from the compounds resulting from the partial hydrolysis of the milk proteins of cultured buttermilk and cottage cheese. Sanders<sup>2</sup> found that four parts of 10 per cent trichloroacetic acid solution to one part of milk was very effective in preparing protein-free filtrates for mineral determinations. Moir<sup>3</sup> used trichloroacetic acid in his study of the distribution of the proteins of milk. Sanders<sup>4</sup> recently reported that trichloroacetic acid in sufficient concentration is almost as efficient as tungstic acid as a precipitant for the nitrogen compound of milk.

## EXPERIMENTAL

### *Cultured Buttermilk*

The procedure that was found satisfactory for cultured buttermilk is as follows:

#### REAGENTS

(a) *Mercuric nitrate*.<sup>5</sup>—Dissolve Hg in twice its weight of HNO<sub>3</sub> and dilute this solution to 25 times its volume with H<sub>2</sub>O. (It is imperative that the reagent be free from the mercurous ion.)

(b) *Picric acid*.—Saturated aqueous solution.

(c) *Trichloroacetic acid*.—20% aqueous solution.

#### PREPARATION OF SAMPLE

If the cultured buttermilk is cold, warm it to approximately 25°C. and stir thoroughly.

#### PROCEDURE

To 10 cc. of the sample, add 10 cc. of the mercuric nitrate reagent. Shake the mixture, allow to stand 5 minutes, and filter through a retentive, medium-fast filter paper (Filtrate No. 1).

<sup>1</sup> *Ind. Eng. Chem. Anal. Ed.*, 4, 418 (1932).

<sup>2</sup> *J. Biol. Chem.*, 90, 755 (1931).

<sup>3</sup> *Analyst*, 56, 228 (1931).

<sup>4</sup> *This Journal*, 16, 140 (1933).

<sup>5</sup> *Methods of Analysis*, A.O.A.C., 1930, 223, 26.

TABLE I.—*Observations recorded in testing commercial cultured buttermilks for gelatin*

SAMPLE	1	2	3	4	5	6
Filtrate from mercuric nitrate (No. 1)	Fairly clear	Fairly clear	Very turbid	Turbid	Turbid	Fairly clear
Aliquot of filtrate No. 1 plus $\frac{1}{2}$ vol. of saturated picric acid	Small amount of flocculent precipitate. Serum clear	Small amount of flocculent precipitate. Serum clear	Colloidal turbidity, no flocs visible	Turbid, no flocs visible	Flocculent precipitate. Serum colloidal turbid	Voluminous flocculent precipitate. Serum clear
Prediction	No gelatin	No gelatin	Gelatin	Gelatin	Gelatin and rennet	No gelatin but rennet
Aliquot of filtrate No. 1 chilled in ice water, plus $\frac{1}{2}$ volume of 20% trichloroacetic acid	Almost clear	Slight opalescence	Turbid	Slightly turbid	Colloidal turbidity	Turbid, (reddish, Millon's reaction)
After standing overnight at 8–10°C., with occasional shaking	Small amount of flocculent precipitate. Serum clear	Small amount of flocculent precipitate. Serum clear	Dense colloidal turbidity	Colloidal turbidity	Flocculent precipitate. Serum turbid (reddish)	Flocculent precipitate. Serum clear (reddish)
Filtrate from trichloroacetic acid mixture heated to 50°C. plus $\frac{1}{2}$ vol. of saturated picric acid (50°C.)	Clear	Clear	Dense colloidal turbidity	Colloidal turbidity	Dense colloidal turbidity	Clear
Conclusions	No gelatin	No gelatin	Gelatin	Gelatin	Gelatin and rennet	No gelatin but rennet
Actual content	Fresh cultured buttermilk—no gelatin	Old cultured buttermilk—no gelatin	Fresh cultured buttermilk plus 2% gelatin	Fresh cultured buttermilk plus 0.1% gelatin	Fresh cultured buttermilk plus 0.15% gelatin plus rennet	Fresh cultured buttermilk plus rennet

To an aliquot of Filtrate No. 1, add  $\frac{1}{2}$  volume of saturated picric acid. Observe the mixture for clearness and type of precipitate. Chill the remainder of the filtrate (No. 1) in ice water, add  $\frac{1}{2}$  volume of 20% trichloroacetic acid, shake well, and allow to stand at 8–10°C. about 16 hours, with occasional shaking particularly during the early part of the period. Observe the filtrate-trichloroacetic acid mixture for clearness and type of precipitate. Filter cold, using a medium-fast filter paper (Filtrate No. 2). Warm the filtrate to 50–55°C., hold at this temperature for at least 5 minutes, and add  $\frac{1}{2}$  volume of warm saturated picric acid (50°C.). Observe while still warm.

Table 1 illustrates what the analyst may expect to observe, and from which he may draw conclusions. It is very evident that the method of Stokes would have led to incorrect conclusions in the case of each sample. When the type of precipitate and the nature of the serum found in conjunction with the Stokes test are considered, the prediction was correct. The use of trichloroacetic acid clearly substantiates the prediction. It should be mentioned that apparently no sample had undergone deterioration. It is recognized that it is not the practice to add rennet to cultured buttermilk, but the possibility of protein hydrolysis occurring during the pasteurization treatment and subsequent culturing procedure is not remote. To be able to distinguish the reactions of rennet from those of gelatin gives the test greater reliability.

The samples referred to in Table 1 and others were tested by the technique of Jacobs and Jaffe.<sup>1</sup> The test proved to be excellent for perfectly fresh samples of cultured buttermilk, but it yielded erroneous results in the case of old samples or those to which rennet had been added. When the filtrates from the basic lead nitrate and charcoal were subjected to the trichloroacetic acid treatment prior to the addition of tannic or picric acid, the results were as definite as those shown in Table 1. The test so modified offers no advantages, however, and it is more laborious than the trichloroacetic acid modification of the Stokes method.

#### COTTAGE CHEESE

The procedure outlined for cultured buttermilk was adapted to cottage cheese by altering the method of preparing the sample, and by a double precipitation with mercuric nitrate. The sample is prepared as follows:

Thoroughly mix 5 grams of cottage cheese with 10 cc. of distilled water at 50–60°C. (a rubber-tipped stirring rod is very satisfactory for this purpose). To this mixture add 5 cc. of mercuric nitrate prepared as indicated previously. Shake, let stand for about 5 minutes, and filter through a medium-fast, but retentive filter paper (No. 40 Whatman paper is satisfactory). To this filtrate add 5 cc. of the mercuric nitrate solution, shake, allow to stand until the precipitate settles, and filter. From this point, proceed as directed previously.

Table 2 illustrates the steps in the procedure, the observations to be made, and the conclusions that may be drawn.

<sup>1</sup> *Loc. cit.*

TABLE 2.—*Observations recorded in testing commercial cottage cheese for gelatin*

SAMPLES	1	2	3	4	5
First filtrate from mercuric nitrate	Slightly turbid	Turbid	Turbid	Turbid	Turbid
2nd addition of mercuric nitrate	Fairly clear	Flocculent ppt. Serum, fairly clear	Flocculent ppt. Serum, turbid	Turbid	Turbid
2nd filtrate	Filters rapidly. Filtrate fairly clear	Filters rapidly. Filtrate fairly clear	Filters slowly. Filtrate, turbid	Filters slowly. Filtrate turbid	Filters slowly. Filtrate turbid
Prediction	No gelatin	No gelatin, but rennet	Gelatin and rennet	Gelatin	Gelatin
‡ vol. of sat. picric acid added to aliquot of 2nd filtrate	Small amount of flocculent ppt. Serum clear	Flocculent ppt. Serum clear	Flocculent ppt. Serum cloudy	Very cloudy	Cloudy
Ppt. on standing	Flocculent, non-adhering	Flocculent, non-adhering	Mixture of non-adhering flocs and adhesive, sticky sediment	Adhesive, sticky sediment	Adhesive, sticky sediment
3rd filtrate	Clear	Clear	Slightly cloudy	Slightly cloudy	Slightly cloudy
Prediction	No gelatin	No gelatin but rennet	Gelatin plus rennet	Gelatin	Gelatin
‡ vol. of 20% trichloroacetic acid added to remainder of 2nd filtrate, and allowed to stand 16 hours at 8–10°C.	Small amount of flocculent ppt. Serum fairly clear	Large amount of flocculent ppt. Serum more or less clear. Reddish coloration (Millon's)	Large amount of flocculent ppt. Serum turbid showing Tyndall effect. Reddish coloration	Small amount of flocculent ppt. Serum very turbid	Small amount of flocculent ppt. Serum turbid
Filtrate(4th) heated to 50° C.	Clear	Clear	Slight colloidal turbidity	Colloidal turbidity	Colloidal turbidity
‡ vol. of sat. picric acid (50°C.) added to 4th filtrate at 50°C.	Clear	Clear	Colloidal turbidity	Colloidal turbidity	Colloidal turbidity
Conclusions	No gelatin	No gelatin but rennet	Gelatin and rennet	Gelatin	Gelatin
Actual content	No gelatin	No gelatin but rennet used in manufacture	0.2% gelatin plus rennet	0.2% gelatin	0.1% gelatin

It is evident that cottage cheese, and more especially that in which rennet has been used in manufacture, contains derived proteins which the mercuric nitrate fails to remove completely, but which are precipitated by picric acid. These precipitates differ in physical characteristics from gelatin-picric acid and thus can be differentiated from the latter. Trichloroacetic acid in the concentration used is effective in removing these derivatives, but not gelatin, with the result that the later addition of picric acid clearly distinguishes between samples that contain gelatin and those that do not contain it.

In an attempt to adapt the method of Jacobs and Jaffe to the testing of cottage cheese, the cheese was mixed with water to give a concentration of milk solids comparable to that of cultured buttermilk in order to observe the conditions specified for the test. The results showed that the method is satisfactory for fresh cottage cheese except when rennet is used in its manufacture. Supplementing the test by the use of trichloroacetic acid failed to give satisfactory results.

In conducting the modified Stokes test, as illustrated in Tables 1 and 2, it is highly recommended, although not absolutely necessary after experience has been gained, that a control sample be included for comparison. The method has also proved successful in connection with sour milk and sour cream in cases where the Stokes test is known to give erroneous results.

#### SUMMARY

In testing cultured buttermilk and cottage cheese for the presence of gelatin by the Stokes method, the addition of picric acid causes a precipitate to be formed even in the absence of gelatin. This is believed to be due to the presence of derived proteins, which the mercuric nitrate fails to remove. When rennet is used in the manufacture of cottage cheese, this precipitate is particularly voluminous.

When one-half volume of 20 per cent trichloroacetic acid is added to the filtrate obtained after precipitating the milk proteins with mercuric nitrate, the derived proteins are caused to coagulate, and may be removed by filtration. When picric acid is added to the filtrate thus obtained, it will remain clear in the absence of gelatin, but will become cloudy in the presence of from 0.1 to 0.25 per cent gelatin. Greater amounts of gelatin result in the formation of a yellow precipitate.

The modification of the Stokes method presented is particularly satisfactory for cream, cultured buttermilk and cottage cheese that contain products derived from the milk proteins by the action of heat, acidification, or primary proteolysis.

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AN APPARATUS FOR THE STUDY OF CHEMICAL REACTIONS UNDER MECHANICAL PRESSURE<sup>1</sup>

By K. C. BEESON and JOHN B. KERSHAW (Fertilizer Investigations, Bureau of Chemistry and Soils, U. S. Department of Agriculture, Washington, D. C.)

The materials used in fertilizers may be grouped into three classes according as they produce an acid, neutral or basic reaction in the soil. The influence of a fertilizer on the soil reaction may bear no relation to the chemical reaction of the material itself. Thus superphosphate that contains an acid salt is neutral as regards its reaction on the soil. Calcium hydroxide and ammonium hydroxide are both basic in a chemical sense and the former is also basic as regards its influence on the soil, but the latter increases soil acidity by nitrification to nitric acid. All ammonium salts, whether acid, neutral or alkaline in chemical reaction, are acid-forming in their influence on the soil, but the nitrates of the alkali and alkaline earth metals, which are usually neutral chemically, have the effect of reducing soil acidity.

It is thus possible by the proper selection of fertilizer materials to prepare complete mixtures that are physiologically neutral. The grades of neutral mixtures that can be prepared from the materials now on the market are limited, however, owing to the large predominance and relatively low cost of the acid-forming materials. The physiological acidity of the average commercial fertilizer has therefore been rapidly increasing during the past few years, as shown in a paper by Mehring and Peterson.<sup>2</sup> If an increase in the acidity of the soil is to be prevented by the use of mixed fertilizers, it will become necessary to increase the use in mixed fertilizers of basic materials such as limestone and dolomite, which do not necessarily contain any one of the three commercial plant food elements.

A study was accordingly undertaken of the feasibility of increasing the use of such materials in mixed fertilizers by studying the reactions that take place between limestone or dolomite and the various components of fertilizer mixtures. It was found that loss of carbon dioxide invariably accompanies the use of these materials in all fertilizer mixtures containing a mono-alkali or alkaline earth phosphate, and that the use of limestone under certain conditions may result in reversion of the phosphoric acid in superphosphate, as well as in loss of ammonia from the ammonium phosphates.

The extent to which these reactions will take place varies with the proportions of the reacting materials, the moisture, the temperature, and the mechanical pressure to which the mass is subjected. The study of these reactions, therefore, required the use of a thermostat and an appa-

<sup>1</sup> Presented at the Annual Meeting of the Association of Official Agricultural Chemists, Washington, D. C., November, 1933.

<sup>2</sup> *This Journal*, 17, 95 (1934).

tus in which the fertilizer mixture could be subjected to mechanical pressure, with means for quantitatively recovering the gases evolved. The apparatus as finally perfected for this purpose is shown in Fig. 1.

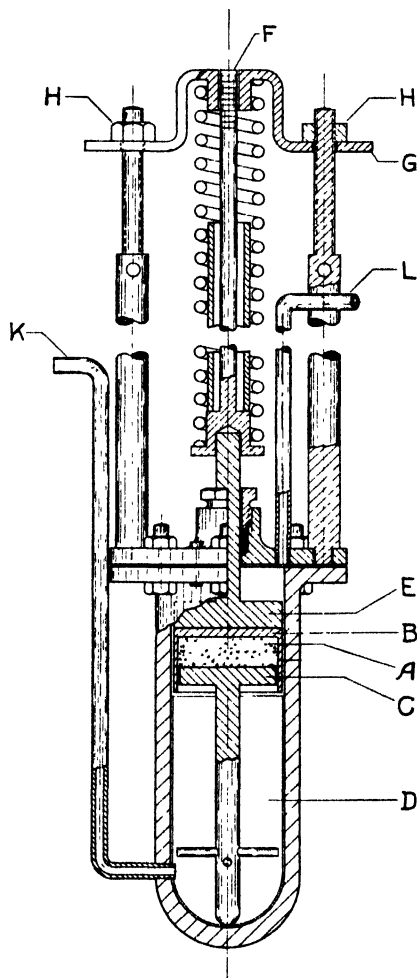


FIG. 1

The mixture, A, to be studied, is placed in the cup B, and the stationary plunger C is inserted. The cup and stationary plunger are then inverted and placed in the bomb D in the position indicated. The piston E is inserted in the bomb, the gasket is placed in position, and the flanges are bolted together. The spring and the graduated pressure gauge F are then placed in position, and the adjusting clamp G and nuts are mounted on the bolts H. When the top of the adjusting clamp is level with the top of the pressure gauge, 30 pounds of pressure is being exerted on the ma-



terial. This is equivalent to 13 pounds per square inch. By turning the nuts clockwise, thus compressing the spring, an increased pressure is obtained and indicated on the graduated gauge. Each scale division denotes an additional 10 pounds of pressure.

The incoming gases pass through the inlet K, and the gases given off are withdrawn through the outlet L. Water or any solution desired may be placed in the bottom of the bomb to keep the desired humidity as nearly constant as possible.

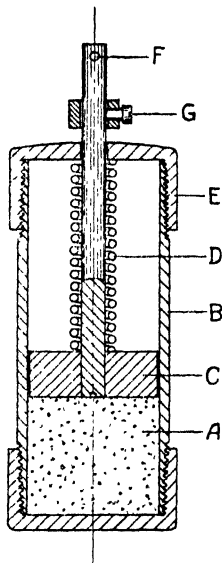


FIG. 2

By varying the size of the cup and the length of the stationary plunger, any quantity of material may be used so long as the depth of the material does not exceed its diameter. All surfaces of the apparatus that come in contact with the reacting material should be tin-lined or made of acid-resisting material to prevent corrosion.

The effect of mechanical pressure on certain reactions can best be followed by an examination of the residual material. In a reaction of this kind the recovery of the evolved gas may be unnecessary, and a simplified modification of the apparatus may then suffice to give the mechanical pressure desired. Fig. 2 shows the design of the apparatus used in a study of the effect of mechanical pressure on the reversion of superphosphate.

The material, A, used in the tests, is placed in the bomb B and tamped down lightly. The piston C is then put in place, and the spring D is clamped down by means of the screw top E. A spring scale is then attached to the apparatus at the point F, and while the bomb is held in place the necessary pull is applied to the spring scale to give a tension in the

spring equal to the mechanical pressure exerted by the spring in the bomb plus the weight of the bomb. At this point the piston shaft begins to move. If the tension indicated on the spring scale minus the weight of the bomb is not equal to the mechanical pressure desired in the bomb the screw cap is adjusted to a new position and the pressure to which the material in the bomb is subjected is again tested. The steps of adjusting the screw cap and testing the resulting pressure are repeated until the desired pressure is obtained. A collar G may be mounted on the piston shaft as shown to indicate whether or not any change in pressure is taking place in the apparatus during the course of the experiment.

## DETERMINATION OF FLUORINE IN PHOSPHATIC MATERIALS, WITH SPECIAL REFERENCE TO THE WILLARD AND WINTER METHOD<sup>1</sup>

By D. S. REYNOLDS (Fertilizer Investigations, Bureau of Chemistry and Soils, Washington, D. C.)

It has been shown by Reynolds and Jacob<sup>2</sup> that the volatilization method<sup>3</sup> for the determination of fluorine, as developed by Wagner and Ross<sup>4</sup> and modified by Reynolds, Ross and Jacob,<sup>5</sup> is not applicable to the analysis of materials, such as phosphate-furnace slags and the Florida waste-pond phosphates, which contain considerable quantities of acid-decomposable silicates. Furthermore, the method requires special reagents and apparatus and, even in the absence of interfering substances, it usually does not account for more than about 93.5 per cent of the fluorine present.<sup>6</sup>

A modification of the lead chlorofluoride method of Hoffman and Lundell<sup>7</sup> was devised by Reynolds and Jacob.<sup>8</sup> It gives much better results for fluorine in phosphatic slags and natural phosphates that contain considerable quantities of acid-decomposable silicates than are obtained by the volatilization method. However, this method, like the volatilization method, does not account for all the fluorine in commercial phosphate rocks, particularly those containing both pyrite and calcium sulfate (for example, the Tennessee blue-rock phosphate). Furthermore, the method is time-consuming and tedious.

The recently developed Willard and Winter method,<sup>9,10</sup> which is based

<sup>1</sup> Presented at the Annual Meeting of the Association of Official Agricultural Chemists, November, 1933.

<sup>2</sup> *Ind. Eng. Chem. Anal. Ed.*, 3, 366 and 371 (1931).

<sup>3</sup> The term "volatilization method" as used in this paper refers to the method which involves the treatment of the sample with concentrated sulfuric acid and the volatilization of the fluorine as silicon tetrafluoride according to the general procedure given in references 4 and 5.

<sup>4</sup> *Ind. Eng. Chem.*, 9, 1116-23 (1917).

<sup>5</sup> *This Journal*, 11, 225-36 (1928).

<sup>6</sup> Reynolds, Ross and Jacob, *This Journal*, 11, 225-36 (1928).

<sup>7</sup> *Bur. Standards J. Research*, 3, 581-95 (1929).

<sup>8</sup> *Ind. Eng. Chem., Anal. Ed.*, 3, 366-70 (1931).

<sup>9</sup> Willard and Winter, *Ind. Eng. Chem., Anal. Ed.*, 5, 7-10 (1933).

<sup>10</sup> Winter and Butler, *This Journal*, 16, 105-7 (1933).

on the treatment of the sample with 60 per cent perchloric acid, the distillation of the fluorine as hydrofluosilicic acid, and the titration of the distillate with thorium nitrate in the presence of zirconium-alizarin indicator, is rapid and requires no special apparatus. Inasmuch as the results reported by Willard and Winter indicate that the method gives reliable results on apatite and commercial phosphate rock, analyses were made to determine whether it could also be used for the analysis of slags and other phosphatic materials which contain acid-decomposable silicates. Also, a brief study was made of the indicator correction necessary in the method, and the effect of varying the volume of the distillate on the recovery of fluorine from certain types of phosphates.

#### INDICATORS IN THE WILLARD AND WINTER METHOD

According to Willard and Winter, the sodium alizarin sulfonate solution is prepared by treating 1 gram of the salt with 100 ml. of ethyl alcohol and adding 150 ml. of alcohol to the filtrate from the undissolved residue. Two parts of this solution are mixed, as needed, with one part of zirconium nitrate solution (1 gram of  $\text{Zr}(\text{NO}_3)_4 \cdot 5\text{H}_2\text{O}$  in 250 ml. of water) and 1-6 drops of the mixture, depending on the volume of the solution to be titrated, are used as an indicator.

A zirconium-alizarin mixture made up in this manner from a certain brand of sodium alizarin monosulfonate was unsatisfactory because of the faintness of the color developed in the fluorine titration. This brand of alizarin was comparatively insoluble in alcohol. A satisfactory solution was prepared, however, by treating 1 gram of the alizarin with 100 ml. of water and adding 150 ml. of ethyl alcohol to the filtrate from the undissolved residue; this solution will be referred to as alizarin solution No. 1. Later, another brand of alizarin was obtained which was sufficiently soluble in alcohol to permit its use in the manner recommended by Willard and Winter; this solution will be referred to as alizarin solution No. 2. The two alizarin solutions gave nearly the same results in fluorine titrations when the proper allowances were made for the blanks, which were different for each solution.

According to Willard and Winter the stock solutions of alizarin and zirconium nitrate are mixed together as needed, and the blank correction for the quantity of fluorine that combines with the indicator is determined by titrating to the disappearance of the color the number of drops of indicator used in the titration with standard fluoride solution. Experiments to determine the effect of the age of the alizarin-zirconium mixture on the blank correction were made by titrating 2 drops of the indicator mixture, contained in 20 ml. of 50 per cent alcohol acidified with 2 drops of 0.1 *N* hydrochloric acid, with 0.01 *N* sodium fluoride. Experiments were also made to determine the effect of the age of the indicator mixture on the total quantity of 0.01 *N* thorium nitrate required for the titration

of 5 ml. of 0.01 *N* sodium fluoride mixed with 5 ml. of water, 10 ml. of alcohol, 2 drops of indicator mixture and 2 drops of 0.1 *N* hydrochloric acid.

The blanks (Table 1) obtained with the indicator mixture prepared from alizarin solution No. 1 increased, in general, with the age of the mixture, particularly with those 3 days old and older. The mixture prepared from alizarin solution No. 2 gave a smaller initial blank than that prepared from solution No. 1; after 1-2 days the two mixtures gave approximately the same results, but after 1 month the No. 2 mixture again gave a significantly smaller blank than did No. 1.

TABLE 1.—*Effect of age of zirconium-alizarin mixture on indicator blank and titration of sodium fluoride by Willard and Winter method*

ALIZARIN SOLUTION	INDICATOR BLANK IN TERMS OF 0.01 <i>N</i> NaF					0.01 <i>N</i> Th(NO <sub>3</sub> ) <sub>4</sub> REQUIRED FOR TITRATION OF 5 ML. 0.01 <i>N</i> NaF				
	AGE OF INDICATOR MIXTURE—DAYS					AGE OF INDICATOR MIXTURE—DAYS				
	0	1	2	3	30	0	1	2	3	30
	ml.	ml.	ml.	ml.	ml.	ml.	ml.	ml.	ml.	ml.
1	0.42	0.48	0.48	0.55	0.71	4.76	4.77	4.82	4.83	4.80
2	0.31	0.47	0.44	—	0.57	4.95	4.91	4.91	—	4.87

These results indicate that the quantity of fluorine adsorbed by or combined with the alizarin-zirconium complex increases with the age of the indicator mixture. Consequently, the total quantity of thorium nitrate required for the titration of a given quantity of sodium fluoride would be expected to decrease with increase in the age of the indicator mixture. The data given in Table 1 show, however, that this is not the case; the consumption of thorium nitrate is approximately constant and is independent of the age of the indicator mixture. It would seem erroneous, therefore, to assume that the blank obtained by simply titrating even a fresh indicator mixture with fluoride solution accurately represents the correction which should be applied in the fluorine determination.

The results of a number of experiments indicated that the errors arising in the determination of the indicator blank by titration can be eliminated by determining the fluorine equivalent of the thorium nitrate titration directly from graphs prepared by plotting milligrams of fluorine against milliliters of the thorium nitrate solution required for the titration of different known quantities of fluorine. In making the analyses, the solutions for titration should have approximately the same volume and should contain the same quantity and age of indicator mixture as the fluoride solutions used in preparing the graphs.

Armstrong<sup>1</sup> recommends the use of a 0.05 per cent aqueous solution of

<sup>1</sup> *J. Am. Chem. Soc.*, 55, 1741-2 (1933).

sodium alizarin sulfonate alone as the indicator, the end point being the appearance of a faint, permanent pink color due to the formation of the thorium lake. This indicator is very satisfactory for the direct titration of soluble fluorides but its sensitivity seems to be affected considerably by the small quantities of silicic acid present in solutions obtained by the distillation of fluorides with perchloric acid.

#### EFFECT OF VOLUME OF DISTILLATE ON RECOVERY OF FLUORINE BY WILLARD AND WINTER METHOD

The data given by Willard and Winter on the distillation of fluorine from sodium fluoride in the presence of gelatinous silica indicate that

TABLE 2.—*Effect of volume of distillate on determination of fluorine by Willard and Winter method*  
(0.1-gram samples for analysis)

MATERIAL	VOLUME OF DISTILLATE	FLUORINE FOUND
	ml.	per cent
Electric phosphoric acid furnace slag No. 983	50	3.10
	75	3.31
	100	3.37
	150	3.45
	200	3.41
Florida waste-pond phosphate No. 726	50	1.98
	75	2.08
	100	2.23
	150	2.25
Tennessee brown-rock phosphate <sup>a</sup>	50	3.36
	75	3.44
	100	3.54
	150	3.53

<sup>a</sup> Bureau of Standards sample No. 56.

it may be necessary to collect more than the customary 50–75 ml. of distillate in order to obtain quantitative recovery of fluorine when acid-decomposable silicates are present. Experiments were therefore carried out to determine the amount of distillation necessary to give the maximum recovery of fluorine from materials such as phosphate-furnace slags and Florida waste-pond phosphate, which contain considerable quantities of acid-decomposable silicates. Experiments were also made with a Tennessee brown-rock phosphate that contained comparatively little silicate.

The results (Table 2) show that 50–75 ml. of distillate is not sufficient to insure the maximum recovery of fluorine from 0.1-gram samples of phosphate slags and waste-pond phosphates; with such materials approximately 150 ml. of distillate should be collected. Furthermore, the results

indicate that at least 100 ml. of distillate should be collected from 0.1-gram samples of phosphate rock. With sodium fluoride, in quantities ranging from 2.66 to 5.70 mg of fluorine, a 99.7 per cent recovery was obtained with 100 ml. of distillate. The comparatively slow evolution of fluorine from the slags and waste-pond phosphates is probably due to the combination of a part of the fluorine with the silicic acid, liberated by the action of perchloric acid on the silicates, to form a nonvolatile silicon oxyfluoride<sup>1</sup> that is only slowly converted into hydrofluosilicic acid.

#### COMPARISON OF METHODS FOR DETERMINING FLUORINE IN PHOSPHATIC MATERIALS

Comparative analyses were made on samples of commercial phosphate rocks, Florida waste-pond phosphates, phosphate-furnace slags, and calcined phosphates. The calcined phosphates were obtained by the action of water vapor and silica on phosphate rock at high temperatures, as described by Reynolds, Jacob and Rader.<sup>2</sup> The analyses by the fusion-acid extraction and the volatilization methods were made according to the methods outlined by Reynolds and Jacob<sup>3</sup> and by Reynolds, Ross and Jacob,<sup>4</sup> respectively.

In making the determinations by the Willard and Winter method the sample of phosphatic material, containing less than 5 mg. of fluorine, was distilled with a solution of 5 ml. of 60 per cent perchloric acid in 20 ml. of water until the temperature of the boiling liquid reached approximately 135°C.; sufficient water was then gradually added to the distilling flask to maintain the temperature between 120° and 150°C., and the distillation was continued until the volume of the distillate amounted to approximately 100 ml. with the phosphate rocks and fluorspar, and about 150 ml. with the waste-pond phosphates and other materials. The distillate was made slightly alkaline to litmus paper with sodium hydroxide, evaporated to a volume of approximately 5-10 ml., and rinsed into a 50-ml. vial to a total volume of approximately 10-12 ml., and 2 drops of the zirconium-alizarin mixture were added. The solution was diluted with an equal volume of ethyl alcohol, 2 drops of 0.1 *N* hydrochloric acid were added in excess of that required to decolorize the indicator, and the fluorine was titrated with 0.06 *N* thorium nitrate. In the case of the fluorspar the distillations were made on 50-mg. samples, and the titrations were made on aliquots of the distillate corresponding to approximately 2.5 mg. of fluorine.

Without exception, the results (Table 3) obtained by the Willard and Winter method on the mineral phosphates and fluorspar were significantly higher than those obtained by the volatilization and the fusion-

<sup>1</sup> Daniel, *Z. anorg. Chem.*, 38, 290-306 (1904); Reynolds and Jacob, *Ind. Eng. Chem. Anal. Ed.*, 3, 371-3 (1931).

<sup>2</sup> *Ind. Eng. Chem.*, 26, (1934)

<sup>3</sup> *Ind. Eng. Chem. Anal. Ed.*, 3, 366-70 (1931).

<sup>4</sup> *This Journal*, 11, 225-36 (1928).

acid extraction methods. Likewise, the Willard and Winter method gave higher results on the calcined phosphates and on the majority of the samples of slag. The lower results given on certain of the slags by the Willard

TABLE 3.—*Comparison of methods for determination of fluorine*  
(Results calculated to moisture-free basis, 105°–110°C.)

SAMPLE NUMBER	MATERIAL	FLUORINE BY—		
		WILLARD AND WINTER METHOD	FUSION-ACID EXTRACTION METHOD	VOLATILIZATION METHOD <sup>a</sup>
		per cent	per cent	per cent
—	Fluorspar <sup>b</sup> + tricalcium phosphate	46.08	44.94	43.14
790	Florida land-pebble phosphate	3.84	3.67	3.71
932	Florida hard-rock phosphate	3.89	3.68	3.66
762	Tennessee brown-rock phosphate	3.71	3.64	3.62
—	Tennessee brown-rock phosphate <sup>c</sup>	3.56	3.33	3.33
930	Tennessee blue-rock phosphate	3.87	3.41	3.55
1031	Tennessee white-rock phosphate	3.85	3.62	3.55
948	Wyoming phosphate	3.49	3.24	3.31
1162	Morocco phosphate	4.24	4.17	3.96
726	Florida waste-pond phosphate	2.33	2.08	1.69
934	Colloidal material from No. 726	1.75	1.61	0.79
727	Florida waste-pond phosphate	2.06	1.94	1.35
915	Florida waste-pond phosphate	1.92	1.84	1.36
1091	Florida soft phosphate	2.40	2.23	1.81
983	Electric phosphoric acid furnace slag	3.45	3.57	1.16
1005	Electric phosphoric acid furnace slag	3.39	3.51	1.50
999	Experimental phosphoric acid blast-furnace slag	0.80	0.69	0.11
1141	Phosphorus blast-furnace slag	1.50	1.19	0.94
1142	Phosphorus blast-furnace slag	1.48	1.09	0.92
—	Calcined phosphate	0.13	0.00	—
—	Calcined phosphate	0.38	0.19	—
—	Calcined phosphate	2.11	2.08	—
—	Calcined phosphate	2.21	2.18	—
—	Calcined phosphate	2.25	2.18	—

<sup>a</sup> Actually determined figures, no correction being applied for failure of the method to give complete recovery of fluorine.

<sup>b</sup> Bureau of Standards sample No. 79, containing 46.19 per cent fluorine.

<sup>c</sup> Bureau of Standards sample No. 56.

and Winter procedure, as compared with the fusion-acid extraction method, may be due to the presence of a portion of the fluorine in forms that are not easily decomposed by perchloric acid; for such materials it may be advisable to fuse the sample with sodium carbonate, as described by Willard and Winter, before making the perchloric acid distillation.

#### SUMMARY

In the Willard and Winter method for the determination of fluorine, the indicator blank, determined by direct titration of the zirconium-

alizarin mixture, increases with the age of the indicator mixture and is higher than the blank existing in the actual fluorine titration. The fluorine equivalent of the thorium nitrate titration is best obtained from the graph derived by plotting milliliters of thorium nitrate solution against milligrams of fluorine, as determined by the direct titration of different known quantities of soluble fluoride. Certain brands of sodium alizarin sulfonate are too insoluble in alcohol to permit of their use in the preparation of the indicator solution recommended by Willard and Winter.

For the maximum recovery of fluorine by the Willard and Winter method approximately 100 ml. of distillate should be collected from samples of commercial phosphate rock, and approximately 150 ml. from samples of phosphate-furnace slag and Florida waste-pond phosphate that contain considerable quantities of acid-decomposable silicates.

The Willard and Winter method is more accurate than either the volatilization method or the fusion-acid extraction method for determining fluorine in mineral phosphates and calcined phosphates; it also gives good results on phosphate-furnace slags.

## A METHOD FOR THE DETECTION OF SOY BEAN FLOUR IN MANUFACTURED FOODS<sup>1</sup>

BY CHARLES H. LAWALL and JOSEPH W. E. HARRISSON (214  
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Manufacturers of soy bean flour, especially those that are offering their product to the baking and sausage industries, make a number of claims for advantages resulting from its use. Some of these claims relating to baked goods are that it improves the flavor, increases the food value, improves the appearance, imparts richness of color, increases the lasting quality of freshness, permits a marked reduction in the amount of shortening and eggs, increases the yield because of greater moisture-holding qualities, makes bread less crumbly, makes pie crust flakier, and improves the palatability of diabetic foods.

The quantities recommended for use range from 2 to 15 per cent of the percentage of wheat flour in the recipe.

In connection with sausage and meat loaf manufacture the use of soy bean is claimed to impart superior binding qualities, improve the flavor, increase the food value, increase the yield, and add no starch.

The quantities of soy flour recommended in these products range from 2 to 10 per cent of the finished food.

As food law enforcement officers the writers are concerned with claims of "increased appearance of richness," "replacement of eggs and butter,"

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<sup>1</sup> Presented at the Annual Meeting of the Association of Official Agricultural Chemists, held at Washington, D. C., November, 1933.



and "increased yields." It has been considered necessary, therefore, to study methods for the detection of soy flour in manufactured products.

The problem was attacked along both chemical and microscopical lines. Soy bean is distinctive in that it contains an enzyme called urease, which may be detected by rather simple qualitative methods. It is also distinctive in showing under microscopic examination certain characteristic cell elements and microchemical reactions.

Urease was discovered by Musculus, in 1874, in urine, and by Takeuchi, in 1909, in soy.<sup>1</sup> The presence of the enzyme has also been reported in small quantities in other leguminous seeds, but not in cereals. Traces of urease have been reported in certain root nodules, seeds, pollens, and flowers.<sup>2</sup> Soy beans differ markedly in their urease content, but the only legume which is reported as containing notable quantities is the jack bean (*canavalia ensiformis*), which has occasionally been grown as a forage crop in the United States, but the seeds of which do not seem to be used either as food or for industrial purposes.

Urease may be detected by a test based upon the fact that under favorable conditions it hydrolyzes urea to ammonia and carbon dioxide, according to the reaction,  $(\text{NH}_2)_2\text{CO} + \text{H}_2\text{O} = 2\text{NH}_3 + \text{CO}_2$ .

The qualitative test applied in this investigation follows:

#### *Litmus and Bromphenol Blue Tests for Detection of Soy Flour*

In a small test tube containing a strip of red litmus paper partly immersed in the liquid, mix approximately 0.5 gram of the sample with 5 cc. of 2 per cent solution of urea; stopper the tube, and heat at 40°C. for 3 hours. If soy is present in more than traces, the litmus paper will be colored blue. (Bromphenol blue may also be used as an indicator, a blue color at the completion of the heating period indicating ammonia liberated by the urease from the urea.)

The reaction described, with soy bean urease as the urea-decomposing factor, has been used for years in the quantitative determination of urea in urine. The writers utilize the same principle, except that the order of the test is reversed.

As it has been reported<sup>3</sup> that 150 mg. of fresh soy bean flour liberates enough ammonia to neutralize 10 cc. of 0.1 N acid, a comparative quantitative test based upon this statement was conducted. The directions follow:

#### *Quantitative Test for Determining Ammonia Liberated by Soy Flour*

Mix 150 mg. of the sample with 10 cc. of 1 per cent urea solution in a test tube and tightly stopper the tube. Keep the temperature of the mixture at 25°C. for 30 minutes, then titrate directly with 0.1 N sulfuric acid, using methyl orange as the indicator.

<sup>1</sup> *J. Coll. Agr. Imp. Univ. Tokyo*, 1909, 1, 1414 (1909).

<sup>2</sup> *J. Am. Chem. Soc.*, 36, 2166 (1914); *Pharm. Z.*, 377 (1920); *Ind. Eng. Chem.*, 15, 793 (1923); *J. Biol. Chem.*, 25, 297 (1916).

<sup>3</sup> *Chem. Weekblad*, 13, 254 (1916).

Comparative tests were made upon a number of cereals and several legumes which were purchased in the unground condition, identified, and subsequently ground. The accompanying table gives the result of the litmus, the bromphenol blue, and the titration tests as applied to five specimens of cereals, four of edible legumes (exclusive of jack beans), eight of whole soy beans, six of commercial soy flours, and one specimen of jack beans. The cereals and legumes were purchased at a food stand in a public market, the whole soy beans from various seed houses, the

SAMPLE	LITMUS TEST	BROMPHENOL TEST	TITRATION TEST
1. Control	—	—	1 drop cc.
2. Barley	—	—	0.10
3. Corn	—	—	0.10
4. Rye	—	—	0.15
5. Oats	—	—	0.20
6. Wheat	—	—	0.20
7. Soup beans	—	+	0.60
8. Lima beans	—	—	0.75
9. French beans	—	—	0.55
10. Greek beans	—	—	0.65
11. Jack beans	+	+	33.10
12. Soy beans, Mammoth Yellow	+	+	19.20
13. Soy beans, Black Wilson	+	+	22.60
14. Soy beans, Black Wilson	+	+	23.00
15. Soy beans, Mammoth Yellow	+	+	20.50
16. Soy beans, Black Wilson	+	+	20.30
17. Soy beans, Manchu	+	+	20.30
18. Michell's Black	+	+	17.90
19. Soy beans, Black Wilson	+	+	21.10
20. Soy Flour No. 1	+	+	10.40
21. Soy Flour No. 2	+	+	8.20
22. Soy Flour No. 3	+	+	3.10
23. Soy Flour No. 4	+	+	9.00
24. Soy Flour No. 5	+	+	4.60

soy flours in original packages either from the manufacturers direct or from fancy grocery houses, and the jack beans were obtained from the Bureau of Plant Industry, United States Department of Agriculture.

Negative results were obtained with the qualitative tests when litmus was used as indicator with all samples of cereals and legumes other than soy. When bromphenol blue was used, these results were confirmed, except in the case of soup beans, when the results were faintly positive.

The titration test showed interesting results. No cereal required more than 0.20 cc. of 0.1 *N* acid, and no legume (excepting soy and jack beans) required more than 0.75 cc. of 0.1 *N* acid. The whole soy beans required a range of from 19.20 to 23.00 cc. of 0.1 *N* acid; and the soy flours from

3.10 to 10.40 cc. The jack beans required the largest quantity, 33.10 cc. of 0.1 *N* acid.

Two facts are clearly apparent from even a cursory study of these results: (1) the litmus test is unfailingly positive when soy flour (and jack bean flour) is used, and (2) the wide range in the results of titration applied to the soy flours precludes the possibility of this test being used for quantitative determinations.

Mixtures of semolina flour and Sample 23 were made up in varying proportions, and the litmus and titration tests were applied. The specimens were made up to a stiff paste or dough as in macaroni manufacture, rolled out into sheets, cut into strips, dried, and ground. The results of these tests follow:

	SAMPLE	LITMUS TEST	TITRATION TEST APPLIED TO 0.5 GRAM
<i>per cent</i>			<i>cc.</i>
100	Semolina flour	—	0.30
95	Semolina flour	+	1.05
5	Soy flour		
90	Semolina flour	+	1.70
10	Soy flour		
75	Semolina flour		
25	Soy flour	+	4.00

Sausage mixtures were then made up with meat (mixture of beef and pork, equal parts) and Sample 24, in varying proportions without the addition of nitrates and without subsequent smoking. The results of these tests follow:

	SAMPLE	LITMUS TEST	TITRATION TEST APPLIED TO 0.5 GRAM
<i>per cent</i>			<i>cc.</i>
100	Ground meat	—	1.70
98	Ground meat	+	1.90
2	Soy flour		
95	Ground meat	+	2.70
5	Soy flour		

The results of these two series of tests confirmed a belief that small quantities of soy flour can be detected when added to such manufactured food products as alimentary pastes and meat products. Tests were made of bakery products (cakes) in which chemical leavening agents had been used, but variable and unsatisfactory results were obtained with the few specimens examined.

A suggestion was made by Howard Gensler, microanalyst of the Pennsylvania Department of Agriculture, that ground soy beans could be detected in peanut butter by the following procedure:

Extract the oil from a portion of the peanut butter by repeated washing with ether by decantation. Dry the residue, place a small quantity (approximately 2 grams) in a small porcelain crucible, and thoroughly mix with a 2% solution of urea. Immediately cover the crucible with a glass microscope slide, on the under side of which is a hanging drop of 10% hydrochloric acid. Allow the apparatus to stand in a warm place overnight. The presence of soy bean is indicated by a marked crystalline residue of ammonium chloride which may be identified by appropriate chemical and physical tests.

With this procedure, even blank or control tests showed a few crystals of ammonium chloride, not to be confused, however, with the heavy deposit noted when soy bean is present. It is believed that these traces of ammonia result from the spontaneous decomposition of the urea solution.

The litmus test gave strongly positive results when applied to a mixture of soy bean and peanut butter, and with a specimen of matzoth in which the manufacturer admitted using 15 per cent of soy meal strongly positive results were obtained by the litmus and bromphenol tests.

When the problem is not complicated by the presence of chemical leavening agents, the results appear to be promising. It may be necessary and feasible in some classes of food products, however, to determine the ammonia by aspiration, such as is used in the Folin method, in which case the evolved carbon dioxide might also be determined, and another element of proof established, except in bakery products in which carbon dioxide might be expected as a normal constituent.

The final and incontrovertible proof of the presence of soy flour is afforded by the characteristic "hour glass," "bobbin," or "spool" shaped cells of the subepidermal layer of the soy bean shown in a microscopic examination.<sup>1</sup> These cells are invariably present in commercial soy flour, but they are sometimes difficult to isolate and identify. The writers have separated these and other distinctive cell tissues and aggregates from all the commercial flours, from experimental mixtures, and from the commercial matzoths by preliminary treatment according to the Schimple method for separating bran tissues from flour.<sup>2</sup>

Professor Wm. J. Stoneback, of the Philadelphia College of Pharmacy and Science, made the following recommendation for this phase of the work:

*Detection of Soy Bean Flour by Macroscopic and  
Microscopic Methods*

1. For a quick macroscopic indicative test make a stiff paste with the flour and 5 per cent of potassium hydroxide solution. A yellow color appearing immediately indicates soy.

<sup>1</sup> Trans. Brit. Pharm. Conf. 1913, 474.

<sup>2</sup> The Microscopy of Vegetable Foods, A. L. Winton, 1906, p. 55.

2. Shake 1 gram of the suspected sample, finely ground, with 10 cc. of petroleum benzene. The presence of soy produces a yellow supernatant liquid and a yellow sediment, proportional to the quantity of soy present. Wheat flour with 5% of soy shows a yellow spotted sediment.

3. Make a paste with concentrated hydrochloric acid. Soy flour quickly develops a lavender color; wheat flour shows the same reaction but much more slowly.

4. Treat soy flour with an aqueous iodine solution. A blue color does not develop. Under microscopic examination the aleurone-containing cells show a yellow or amber color. With this same treatment wheat flour turns blue immediately. In mixtures of soy flour and wheat flour, treated in this manner, a two-colored field is visible, the soy particles being yellow and the wheat particles blue.

5. For complete identification locate the characteristic subepidermal cells.

### SUMMARY

A chemical method and a microscopical method for detecting soy flour in certain commercial food products are presented. The first is based upon the presence of urease and the second upon the distinctive cell elements in soy. Tests of the common cereals and a number of legumes were made. The chemical test proposed gives satisfactory results for the detection of soy flour in alimentary pastes, meat products, and unleavened bread.

### SUPPLEMENTARY NOTES ON THE PERFECTED CHROMIC ACID METHOD FOR DETERMINING ORGANIC CARBON

By J. W. WHITE and F. J. HOLBEN (The Pennsylvania State College, State College, Pa.)

Data published at the time this method was first proposed<sup>1</sup> show conclusively that organic materials are capable of complete oxidation in a boiling mixture of sulfuric and chromic acids. The introduction of a sulfur trioxide (SO<sub>3</sub>) absorption tube, used for the first time in this method greatly simplifies the usual analytical procedure pertaining to such wet combustion methods.

The following notes supplementary to the original paper, based on nine years of experience with the method, are offered as a guide in regard to the technic and certain precautions found necessary.

*Sulfur trioxide (SO<sub>3</sub>) absorption tube.*—The success of the method is dependent upon the efficiency of the SO<sub>3</sub> absorption tube. Coarse glass wool selected at random is unsuitable because coarse and often brittle glass wool fails to retain a sufficient volume of the constant boiling-point sulfuric acid in the arms of the absorption tube. The glass wool found suitable by the writers for this purpose is that sold by Arthur H. Thomas, Philadelphia, Pa., as "Glass Wool—Fine Lead and Borax Free." Glass beads or fine pumice are unsuitable as substitutes for glass wool. Before the upper right-hand plug is inserted, the constant boiling-point acid

<sup>1</sup> *J. Ind. Eng. Chem.*, 17, 83 (1925).

(98.33 per cent) is run from a buret drop by drop into each arm of the tube until the glass wool is thoroughly drenched. The excess of acid is allowed to drain into the bottom of the tube between the two plugs of glass wool. Sufficient acid should be added to fill the space at the bottom of the tube one-third full (12–15 cc. of acid is sufficient to saturate the glass wool and provide for the excess indicated). The lower right-hand plug is then pushed downward until it comes in contact with the excess of acid. The left-hand plug should also be in contact with the acid in the bottom of the tube. The upper right-hand plug of untreated glass wool is then inserted, care being taken to leave a space of 2.5 cm. between the two plugs. This precaution is necessary to prevent the acid from being carried over into the second tube during the passage of air through the

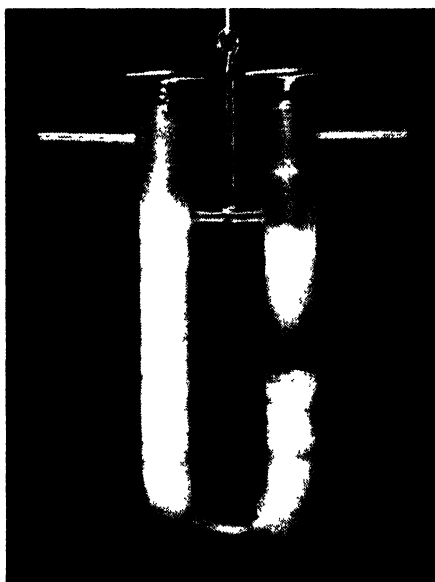


FIG. 1.— $\text{SO}_2$  ABSORPTION TUBE CONTAINING FINE SPECIALLY PREPARED GLASS WOOL DRENCHED WITH CONSTANT BOILING-POINT SULFURIC ACID

train of tubes. The tube thus prepared may be used continuously until the volume of acid is sufficient to fill the space at the bottom of the tube.

*Aspirator used.*—The usual bottle aspirator (20 liters capacity) is recommended rather than the type shown in the illustration of the original publication. The end of the glass outlet tube through which the water flows from the bottle should dip below the surface of water contained in a beaker or other suitable vessel in order to prevent back pressure through the apparatus.

*Procedure.*—Place from 1 to 3 grams of soil or 0.2 to 0.3 gram of high carbon material in generating flask M. Before attaching the generating

flask to the apparatus (P), moisten with a drop of water the ground-glass surface of (P), to which the flask is fitted. (This precaution is necessary to prevent the flask from sticking to the apparatus.) After attaching generating flask (M), start the suction and open all valves except the delivery valve C<sup>1</sup>. Run 10 cc. of the stock chromic anhydride solution into the generating flask after first attaching tube K to L, then run 50 cc. of sulfuric acid (sp. gr. 1.83–1.84) into the generating flask in a similar manner. After the sulfuric acid has drained through the delivery valve C<sup>1</sup>, slightly remove the valve just sufficiently to allow the ground-glass surface to become lubricated with a drop of the acid. (The valve should be revolved several times to insure thorough distribution of the acid over the entire ground-glass surface. This procedure is necessary to prevent the valve from sticking.) Close valve C<sup>1</sup> and bring the solution in the generating flask to a boil. Now open valve C<sup>1</sup> slowly and boil for 30 minutes, during which time at least 1.5 liters of CO<sub>2</sub> free air is drawn through the apparatus. Remove the flame and continue the aspirating for several minutes before detaching the generating flask. The U-tube valves are then closed, and tubes G and H are removed, wiped, and weighed after a lapse of 15 minutes. The combined weight of these two tubes, corrected for the blank, gives the total carbon or CO<sub>2</sub>. (Inorganic CO<sub>2</sub> may be determined by means of the same apparatus by using 50 cc. of a 10 per cent solution of phosphoric acid.) Potassium bichromate should not be substituted for chromic anhydride (CrO<sub>3</sub>) because the former has been found to contain carbon that is removed only with great difficulty.

## COLORIMETRIC METHOD FOR DETERMINATION OF ROTENONE

By C. R. GROSS and C. M. SMITH (Insecticide Division, Bureau of Chemistry and Soils, U. S. Department of Agriculture, Washington, D. C.)

The Jones<sup>1</sup> method for the determination of rotenone by extracting with carbon tetrachloride and weighing as C<sub>22</sub>H<sub>22</sub>O<sub>6</sub> · CCl<sub>4</sub> has proved very serviceable. It is, however, inapplicable to products containing a small quantity of rotenone, and furthermore, it requires considerable time. The desirability of developing other quantitative methods is therefore obvious.

No procedure has been developed to make the blue color of the Durham qualitative test for rotenone<sup>2</sup> sufficiently permanent to allow its use for quantitative purposes. Several other color reactions are described in the literature, but none of them appears to be particularly promising.

<sup>1</sup> *Ind. Eng. Chem. Anal. Ed.*, 5, 23 (1933).

<sup>2</sup> *Ibid.*, 75.

However, the senior author has discovered a red color reaction which has been successfully employed as the basis of a new colorimetric method. This reaction occurs when an acetone solution of rotenone is treated first with alcoholic potash and then, after a suitable interval, with a nitric acid solution containing a little sodium nitrite. The chemical reactions involved have not been studied, but the method based on this procedure has proved very useful for determining rotenone in samples not containing isorotenone, deguelin or dihydrorotenone—the only other compounds known to respond to the test.

The method gives unduly high results for the rotenone content of derris and cube extracts due to the presence of deguelin and perhaps to other extractives not yet identified as giving the test. Investigations now in progress indicate, however, that these results, computed as rotenone, will aid in attempts being made to correlate chemical composition with insecticidal effectiveness.

#### REAGENTS

(1) *Alcoholic potash*.—10 grams of potassium hydroxide+100 cc. of 95% ethyl alcohol. The solution should be freshly prepared, clear, and colorless.

(2) *Nitric acid-sodium nitrite*.—1 volume of  $\text{HNO}_3$  CP + 1 volume of aqueous sodium nitrite solution containing 0.25 gram of  $\text{NaNO}_2$  per liter.

#### PROCEDURE

From the sample being analyzed, prepare an acetone solution containing 0.05 to 0.30 mg. of rotenone per cc. and pipet a 2 cc. aliquot of this solution into a dry test tube. (Use thin-walled tubes of matched internal diameter.) Add 2 cc. of the alcoholic potassium hydroxide solution, and mix. Place the test tube in a water bath at  $20^\circ\text{C}$ . for exactly 2 minutes, then add 6 cc. of the nitric acid-sodium nitrite reagent. Stopper the tube, quickly mix the contents, and cool to  $20^\circ\text{C}$ . by continuous agitation of the tube in the water bath for at least 30 seconds. Let stand in the water bath for 15 minutes to develop the maximum color. Within the next 30 minutes evaluate the color by comparison with standards prepared at the same time from known quantities of pure rotenone.

*Notes*.—The rotenone to be determined must be in acetone solution, because other common organic solvents, including the closely related methyl ethyl ketone, do not give satisfactory results.

The initial reaction will not proceed if much water is present. Alcohol of 95% strength has been specified for the alcoholic potash, but introduction of additional water through the use of wet containers must be avoided and the acetone solution of rotenone should be practically free of water.

Very little change in color occurs for 15 to 45 minutes after mixing; to obviate any effect of change in color, the color standards should be prepared at approximately the same time as are the unknowns being evaluated.

The tubes should be emptied soon after being read because if they stand for several hours vigorous reaction between the nitric acid and the organic solvents occurs and the contents boil over.

#### SPECIFICITY OF TEST

Of the primary compounds that have been found associated with rote-



none in plants (deguelin, toxicarol, tephrosin and isotephrosin), only deguelin gives the color test.

Dihydorotenone also gives colors identical with those from rotenone. This compound has not been encountered in plant material, but because of its greater stability and recognized insecticidal properties may be incorporated in commercial insecticides in the future.

The primary decomposition products of rotenone and deguelin, namely, dehydrototenone, rotenonone and dehydrodeguelin, do not give any red color.

The test is not given by nicotine or pyrethrum extract, either of which might be encountered in association with rotenone in proprietary insecticides.

#### PRACTICAL APPLICATION

Some examples illustrating practical applications follow:

Of eight samples of commercial rotenone analyzed by polarimetric and gravimetric methods, seven gave practically identical results at 86 per cent; the other showed 65 per cent. The new method gave seven results ranging from 85 to 90 per cent, and one result of 82 per cent, the latter being obtained on the sample known to contain the least rotenone.

Six subsamples were taken from a mixture of 1 per cent rotenone and 99 per cent diatomaceous earth in order to test the thoroughness of mixing. The new method gave results ranging from 0.94 to 0.99 per cent, the average being 0.98 per cent.

The results given indicate a satisfactory agreement between the gravimetric method and the red colorimetric method for analyzing dry powdered samples containing rotenone unaccompanied by other extractives.

When the colorimetric method was used for the analysis of four samples of powdered derris and five of powdered cube, the results for rotenone were 50 to 100 per cent higher than those obtained on the same samples by Jones with his gravimetric method. The higher results are probably due to the deguelin content of the samples although these investigations have not definitely excluded the possibility that other unidentified extractives may be contributing factors. It may be stated that the results, although high, never exceeded 75 per cent of the figure for total extract.

One of the practical applications of the method should be the estimation of rotenone spray residues on fruits and foliage. Tests of the method for this purpose were made on four samples each of peaches, peach leaves, and apple leaves that had been sprayed with rotenone and with derris both with and without the addition of oil as a sticker. These samples were analyzed several weeks after being sprayed. The acetone solution was prepared by rinsing the fruits or leaves one by one with a fine jet of acetone from a wash bottle. Rotenone was found only on the samples on which oil had been used, the peaches showing from 7 to 30 mg. per fruit and the leaves from 1 to 5 mg. per leaf. The results for derris spray

residues were higher than those for rotenone residues. There is no way of verifying these results, but they appear to be logical.

### SUMMARY

A method is presented for the colorimetric estimation of rotenone alone or when present with non-interfering substances. Its optimum range is from 0.05 to 0.30 mg. per cc. of acetone solution.

When this method was applied to derris or cube roots the result obtained was 50–100 per cent higher than the result for rotenone alone determined gravimetrically. This higher result can be attributed to the presence of deguelin, although unidentified compounds present in such extracts might be involved.

A few applications of the method are described.

## A STUDY OF THE KJELDAHL METHOD\*

### III. FURTHER COMPARISONS OF SELENIUM WITH MERCURY AND WITH COPPER CATALYSTS<sup>1</sup>

By R. A. OSBORN and ALEXANDER KRASNITZ (Food Research Division,  
Bureau of Chemistry and Soils, U. S. Department of Agriculture,  
Washington, D. C.)

An earlier paper<sup>2</sup> contains data relating to the comparative effectiveness of selenium, mercury, and copper as catalysts in the Kjeldahl method for the determination of nitrogen. With flour samples, it was found that mercury and selenium were about equally efficient, that copper sulfate was slower, and that a combination of selenium with mercuric oxide or with copper sulfate was most effective. Taylor<sup>3</sup> and Hitchcock and Belden<sup>4</sup> have since reported that mercury and selenium together as catalysts are more effective than is either when used alone. In view of these reports, the writers considered it to be desirable to extend their study to include all classes of substances mentioned as subject to Kjeldahl analysis in Official and Tentative Methods of Analysis of the Association of Official Agricultural Chemists.

The results of this study are summarized in Table 1. In Column A will be found the nitrogen content of each of eighteen samples determined by the official K.G.A. procedure<sup>5</sup> with mercuric oxide as the catalyst and a 2-hour digestion period. In Column B are results obtained by using a mixture of mercuric oxide and selenium and a digestion period of 2 hours.

\* Food Research Division Contribution No. 222.

<sup>1</sup> Presented at the annual meeting of the Association of Official Agricultural Chemists, Washington, D. C., November, 1933.

<sup>2</sup> *This Journal*, 16, 110 (1933).

<sup>3</sup> *Ind. Eng. Chem. Anal. Ed.*, 5, 263 (1933).

<sup>4</sup> *Ibid.*, 402.

<sup>5</sup> *Methods of Analysis*, A.O.A.C., 1930, 21.

In Column C are the results of analyses with mercuric oxide and selenium catalysts and a digestion period equal to 1.5 times the clearing time, expressed in minutes. In Columns D, E, and F, respectively, will be found the nitrogen content of these samples obtained by using mercuric oxide catalyst, copper sulfate plus selenium catalyst, and selenium catalyst alone, and a digestion period in each case 1.5 times the clearing time. All results are averages of duplicate determinations. In all cases the following quantities of catalysts and reagents were used: mercuric oxide, 0.7 gram; selenium, 0.1 gram; copper sulfate hydrate, 1.0 gram; anhydrous sodium sulfate, 15.0 grams; and concentrated sulfuric acid, approximately 25 ml. All digestions were started on cold 400-watt calibrated heaters, which did not differ materially in their power output.

If the values indicated in Column A are considered as standard, the results in Columns B, C, and D are satisfactory and those in Columns E and F are low. Low results should be considered as due to incomplete digestion of the samples rather than to loss of nitrogen by volatilization. The values in Column B (Se + HgO — 2hr) are on the average a trifle lower (1 per cent of the nitrogen content of the samples) than those in Column A, but this difference is not large. The fact that the nitrogen values in Columns C and D are in close agreement with the values in Column A makes possible a direct comparison of the catalytic speed of mercuric oxide plus selenium and that of mercuric oxide alone. If the soft coal sample, which foamed with the mercuric oxide catalyst, retarding the rate of digestion, and the crude sugar sirup sample, which gave a low nitrogen value with mercuric oxide catalyst, indicating incomplete digestion, are omitted from this comparison, the saving in time of C over D is almost 25 per cent.

It is apparent from the data in Column E that copper sulfate plus selenium is not so effective as mercuric oxide plus selenium or as mercuric oxide alone. Contrary to the claim of Lauro<sup>1</sup> the writers found that under the conditions of this study selenium alone was inferior to mercuric oxide alone. Samples may clear more quickly with selenium than with mercury, but the degree of conversion to the ammonium salt is less. Data submitted by the Associate Referee on Nitrogen (see p. 246) are consistent with these results.

Davis and Wise<sup>2</sup> and Sandstedt<sup>3</sup> state that the use of selenium as a Kjeldahl catalyst may lead to low results when intense digestion heats (550- to 600-watt electrical heaters) are used or when the digestion period is extended. It has long been known<sup>4</sup> that an insufficient excess of sulfuric acid for the digestion results in loss of nitrogen. Therefore a study was also made to determine whether a relationship exists between nitrogen

<sup>1</sup> *Ind. Eng. Chem. Anal. Ed.*, **3**, 401 (1931).

<sup>2</sup> *Cereal Chem.*, **10**, 488 (1933).

<sup>3</sup> *Ibid.*, **9**, 156 (1932).

<sup>4</sup> P. A. W. Self, *J. Pharm.*, **88**, 384 (1912)

TABLE 1.—Comparison of catalysts in the Kjeldahl nitrogen method

SUBSTANCE ANALYZED	A			B			C			D			E			F		
	HgO CATALYST			HgO AND Se CATALYST			HgO AND Se CATALYST			HgO CATALYST			CuSO <sub>4</sub> AND Se CATALYST			Se CATALYST		
	WEIGHT OF SAMPLE	TIME OF DIGESTION		TIME OF DIGESTION	N		TIME OF DIGESTION <sup>1</sup>	N		TIME OF DIGESTION <sup>1</sup>	N		TIME OF DIGESTION <sup>1</sup>	N		TIME OF DIGESTION <sup>1</sup>	N	
		min.	per cent		min.	per cent		min.	per cent		min.	per cent		min.	per cent		min.	per cent
Milk (cows)	5.15	120	0.551	120	0.544	0.544	60	0.550	75	0.545	68	0.536	75	0.537	75	0.537		
Spaghetti	1.000	120	2.17	120	2.17	2.17	42	2.16	50	2.17	45	2.05	48	2.09	48	2.09		
Egg noodles	1.000	120	2.44	120	2.44	2.44	35	2.43	54	2.43	38	2.37	45	2.37	45	2.37		
Soft coal	2.000	120	1.16	120	1.20	1.20	53	1.17	113 <sup>2</sup>	1.18	65	1.06	68	1.08	68	1.08		
Meat (round steak)	1.000	120	3.89	120	3.88	3.88	35	3.91	50	3.88	38	3.85	41	3.78	41	3.78		
Bouillon cubes	1.336	120	2.59	120	2.57	2.57	45	2.57	55	2.57	47	2.56	48	2.57	48	2.57		
Prepared mustard	5.000	120	0.78	120	0.76	0.76	60	0.77	78	0.78	63	0.77	66	0.76	66	0.76		
Dried whole egg	1.000	120	7.08	120	7.01	7.01	52	7.10	60	7.10	52	6.90	52	6.97	52	6.97		
Crude sugar sirup	6.100	120	0.00245	120	0.00231	0.00231	48	0.00245	45	0.00214	60	0.00210	60	0.00224	60	0.00224		
Rawhide	1.000	120	15.86	120	15.71	15.71	38	15.87	45	15.83	38	15.61	38	15.66	38	15.66		
Tanned leather	1.000	120	8.00	120	7.97	7.97	30	8.03	45	7.90	33	7.93	38	7.96	38	7.96		
Linseed meal feed	1.000	120	5.55	120	5.53	5.53	45	5.54	60	5.55	55	5.48	55	5.45	55	5.45		
Mixed feed	1.000	120	2.97	120	2.98	2.98	32	2.92	41	3.00	38	2.86	38	2.88	38	2.88		
Molasses feed	1.000	120	2.88	120	2.89	2.89	45	2.90	45	2.88	45	2.83	45	2.86	45	2.86		
Soybeans	1.000	120	6.66	120	6.53	6.53	38	6.66	60	6.67	42	6.57	45	6.54	45	6.54		
Ammoniated lignin	0.500	120	8.92	120	8.80	8.80	35	8.74	45	8.70	42	8.71	45	8.66	45	8.66		
Fertilizer 6-6-5	1.000	120	3.45	120	3.41	3.41	30	3.43	40	3.45	30	3.31	40	3.41	40	3.41		
Gluten flour	1.000	120	7.87	120	7.73	7.73	30	7.85	45	7.79	30	7.76	38	7.75	38	7.75		

<sup>1</sup> Clearing time X 1.5.<sup>2</sup> Sample foamed with HgO catalyst. No foaming with selenium.

values obtained with the selenium catalyst plus long digestion, and the volume of acid used. Duplicate determinations were made on 1-gram samples of a linseed meal feed, dried eggs, and a rawhide with mercuric oxide and selenium catalyst singly and in combination, with periods of digestion of 2 hours and 5 hours upon 400-watt heaters. Results of this study are given in Table 2. Satisfactory nitrogen values for the samples are shown for all 2-hour runs and for the 5-hour runs with mercuric oxide. Low values were obtained with 5-hour digestions with selenium and with selenium and mercuric oxide when 25 ml. of sulfuric acid was used. The use of larger quantities of acid (37 ml. and 50 ml. ) prevented loss of nitrogen upon long digestion of the samples with the mixed catalyst. This would indicate that there is greater danger of loss of nitrogen upon digestion with selenium alone or with selenium in combination with mercuric oxide than with mercuric oxide alone, but that this loss can be largely if not entirely eliminated by the use of somewhat larger quantities of sulfuric acid.

#### SUMMARY

A wide variety of substances was analyzed for nitrogen by the Kjeldahl method in order to determine the relative catalytic speed of selenium, mercuric oxide, selenium with mercuric oxide, and selenium with copper sulfate. Selenium with mercuric oxide gave the same results as mercuric oxide alone, with a saving in time of about 25 per cent. Selenium used alone or in combination with copper sulfate was less effective than the mercuric oxide catalyst.

When the digestion period is extended the danger of loss of nitrogen increases in the following order: mercuric oxide, selenium, and mercuric oxide plus selenium. The danger can be obviated by using larger quantities of sulfuric acid.

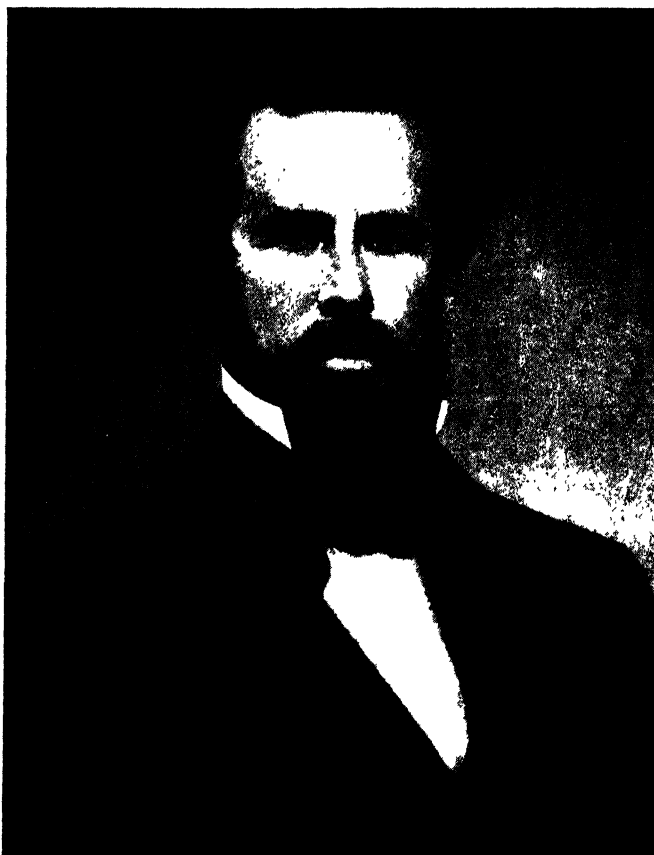
TABLE 2.—*Effect of digestion period and volume of sulfuric acid on nitrogen results*

CATALYST	DIGESTION TIME	VOLUME H <sub>2</sub> SO <sub>4</sub> .	LINSEED MEAL	DRIED EGGS	RAWHIDE
	<i>hours</i>	<i>ml.</i>	<i>per cent</i>	<i>per cent</i>	<i>per cent</i>
HgO	2	25	5.58	7.10	15.46
HgO	5	25	5.51	7.09	15.50
Se	2	25	5.56	7.15	15.47
Se	5	25	5.31	6.80	14.70
HgO+Se	2	25	5.53	7.03	15.31
HgO+Se	5	25	5.22	6.00	14.46
HgO+Se	5	37	5.56	7.10	15.34
HgO+Se	5	50	5.58	7.09	15.46

## BOOK REVIEW

**Food Products.** By HENRY C. SHERMAN, Ph.D., Sc.D., Mitchill Professor of Chemistry, Columbia University, Third edition, completely rewritten. Pp. xii+674, 42 figures. The Macmillan Company, New York, 1933. Price \$3.00.

The present third edition of Sherman's well-known "Food Products" brings the subject matter of the previous edition of this excellent work completely up to date with an increase in the number of chapters from thirteen to fifteen. The first two chapters of the volume are general in character and deal with "The Principal Constituents and Functions of Food" and "General Aspects of Food Control." Then follow twelve special chapters dealing with "Milk," "Milk Products other than Butter," "Eggs," "Meats and Meat Products," "Poultry, Game, Fish and Shellfish," "Grain Products," "Vegetables," "Fruits and Fruit Products," "Nuts," "Edible Fats and Oils," "Sugars, Sirups and Confectionery" and "Food Adjuncts, Unclassified Food Materials, and Extra Foods." A final chapter deals with "Some Aspects of Food Economics." Appendices A and B give the texts of the Federal Food and Drugs Act and Meat Inspection Act with excerpts from various regulations pertaining thereto. Appendix C gives a table of the percentages of calcium, phosphorus, iron, copper and manganese in 144 common foods. Appendix D gives a table of the comparative content of vitamins A, B, C, and G in 179 common foods. Each chapter contains at the end an extensive bibliography of reference works for suggested collateral reading. As a convenient general work supplying valuable information upon the chemical composition, nutritive value, technology, marketing, regulatory control and economics of foods, Sherman's "Food Products" is indispensable whether to the student, research chemist, regulatory official, nutrition expert or manufacturer.—C. A. BROWNE.



DR. JAMES HIGGINS

1818-1870

*First State Agricultural Chemist of Maryland*

1848-1858

(See page 474)

## SECOND DAY

### TUESDAY—MORNING SESSION—Continued

#### REPORT ON DAIRY PRODUCTS

By GUY G. FRARY (State Chemical Laboratory,  
Vermillion, S. D.), *Referee*

Reports of the Associate Referees on Cheese, Malted Milk, Milk Proteins, Dried Milk and Ice Cream were received. The recommendations of the Associate Referee on Cheese are approved, as are also the recommendations of the Associate Referees on Dried and Malted Milks, and Milk Proteins. The Associate Referee on Butter was unable to carry out the recommendations for study made last year. The associate referees have made a creditable showing and to them and the other workers who have collaborated so well and so willingly the Association is indebted.

In connection with the report of the Associate Referee on Milk Proteins it will be seen that two methods, apparently of equal accuracy, are available for the measure of casein and of albumin in milk products. In *Methods of Analysis* there is one good method for each determination, and the Associate Referee reports satisfactory results with two other methods. The results of collaborative work do not show that the proposed methods excel, either in accuracy or ease or time of manipulation, the present methods. It is the opinion of the Referee that there should not be more than one official method for a determination unless some definite difference in the two methods is evident, for example, between volumetric and gravimetric methods, or in apparatus required. In the case of the proposed method for casein there is no such difference, and the method presented is more time-consuming and laborious than the present official method. The Association last year took final action on the deletion of the second of the two official methods for albumin in milk,<sup>1</sup> and there does not appear to be sufficient justification at this time for the insertion of a second official procedure for this determination. As collaborative work has shown that results obtained by the present official method are in close agreement with those obtained by the proposed method, and the present method is the simpler of the two, a selective recommendation should be made next year.

In *Methods of Analysis* are also found two official methods for the determination of fat in cheese.<sup>2</sup> It appears that the first of these is seldom used and is not to be preferred over the second, or the Schmid-Bondzynski method. It is, therefore, recommended that the Associate Referee on Cheese be instructed to study the advisability of deleting the first, or "gravimetric method" and bring in a report on this matter in 1934.

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<sup>1</sup> *This Journal*, 16, 61 (1933).

<sup>2</sup> *Methods of Analysis*, A.O.A.C., 1930, 239.



During the year there was received a criticism of the present method for the qualitative determination of gelatin in dairy products<sup>1</sup> to the effect that the test was found uncertain when applied to sour cream and that it frequently gave positive results when no gelatin was present. In 1927 Hall<sup>2</sup> reported on this test and referred to its uncertainty when applied to evaporated milk and especially to sour milk. The modification of the method proposed by Seidenberg<sup>3</sup> was given, and it was recommended that the matter be assigned for collaborative work. This recommendation was repeated each year by Committee C but no work was undertaken, or reported, and in 1931 the Committee recommended that the study of qualitative tests be dropped "for the present."

Time has permitted only a small amount of work to be done on this subject by the Referee this year, but W. L. Roberts of the North Dakota Regulatory Department, Bismarck, collaborated and confirmed the lack of clearness in the present method. His experiments and those carried on under direction of the Referee show that with sour cream the method as now printed is uncertain. The Referee's work confirms Robert's following statement: "Gelatin in sour cream is easily detected without Seidenberg's modification. The precipitates, so similar at formation, are so dissimilar physically after vigorous shaking that differentiation is not difficult. The protein picrate of sour cream becomes gelatinous and sinks to the bottom, similar to  $\text{Al}(\text{OH})_3$  except for color, while gelatin picrate agglomerates into sticky masses which either float or stick to the sides of the test tube." Although this statement is true for those familiar with the test, it is also evident that the test is misleading to one trying it for the first time or only at rare intervals, and the last sentence of the method<sup>4</sup> is not accurate when the products are sour, and in some cases it is not true with fresh products.<sup>5</sup> Jacobs and Jaffe<sup>6</sup> studied this problem last year and obtained encouraging results. This subject has been held in abeyance too long, and it is recommended that the Associate Referee on Milk be instructed to bring in a recommendation for a revised qualitative test for gelatin.

A communication from L. D. Haigh, Columbia, Mo., directed the attention of the Referee to an apparent error in the formula for a clarifying solution to be used in the determination of lactose in milk.<sup>7</sup> The method calls for 20 cc. of glacial acetic acid in the mercuric iodide solution, although it appears that 200 cc. should be used. Haigh stated that he had prepared the solution as directed and found it unsatisfactory.

The method had been printed without change since 1904. In the origi-

<sup>1</sup> *Methods of Analysis*, A.O.A.C., 223.

<sup>2</sup> *This Journal*, 11, 299 (1926).

<sup>3</sup> *J. Ind. Eng. Chem.*, 5, 927 (1913).

<sup>4</sup> *Methods of Analysis*, A.O.A.C., 1930, 223, 26.

<sup>5</sup> Hall, *Loc. cit.*

<sup>6</sup> *Ind. Eng. Chem. Anal. Ed.*, 4, 418 (1932).

<sup>7</sup> *Methods of Analysis*, A.O.A.C., 1930, 216, 12.

nal publication<sup>1</sup> the formula calls for ten times the proportion of acetic acid shown in *Methods of Analysis*, and it was found by Haigh that the solutions made of that strength gave satisfactory results. Through the kind assistance of Leslie Hart, the reference to the literature was confirmed, and the Referee found that in an article published the same year by Harvey W. Wiley<sup>2</sup> the error as to the proportion of acetic acid occurred. The evidence of error being quite conclusive, it is recommended that it be referred for correction to the Committee on Editing Methods of Analysis. As the method as now printed calls for a large volume of the mercuric iodide solution and it appears that if the solution were made with the amount of acetic acid originally intended a lesser volume should suffice to precipitate the milk proteins, it is recommended<sup>3</sup> that the method for lactose be referred to the proper referee for study.

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No report on butter was given by the associate referee.

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## REPORT ON SODIUM CHLORIDE IN CHEESE

By CARL B. STONE (U. S. Food and Drug Administration,  
Minneapolis, Minn.), *Associate Referee*

Following personal correspondence with G. P. Sanders<sup>4</sup> the Associate Referee thought it necessary to test out the possible loss of salt that occurs in the ashing of cheese by the present official method. Sanders submitted figures on different types of cheese showing that a decided loss of salt occurred in ashing by the present official method. Adding sufficient base in order to neutralize acidity in the cheese reduced this loss and gave a much higher salt figure on ashing the sample by the official method. A modified Volhard procedure by Munchberg<sup>5</sup> is another method used by Sanders which gave very good results.

Comparison of this method with ashing, with and without an added base, are described by Meyer,<sup>6</sup> and also by McDowall et al.<sup>7</sup> The results obtained by these workers show that the modified Volhard method yields reliable results.

In order to check this problem thoroughly several different types of cheese were analyzed by the collaborators by the following three methods.

- (1) Official method, for ash and salt. *Methods of Analysis*, A.O.A.C., 1930, 239.
- (2) Use the same official method but place 0.5 gram of either calcium acetate or sodium carbonate in the ashing dish with the cheese, plus some water. Place dish

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<sup>1</sup> *J. Pharm. Chim.*, 10, 108 (1884).

<sup>2</sup> *Am. Chem. J.*, 6, 289 (1884).

<sup>3</sup> For report of Subcommittee C and action of the Association, see *This Journal*, 17, 56 (1934).

<sup>4</sup> Bureau of Dairy Industry, Washington, D. C.

<sup>5</sup> *Milchwirtschaft. Zentr.*, 59, 201 (1930).

<sup>6</sup> *Milchwirtschaft. Forsch.*, 10, 231 (1930).

<sup>7</sup> *J. Dairy Research*, 2, 184 (1931).

on the steam bath to drive off the moisture and then ash the sample according to the official method. Run the chlorides in both cases by the Volhard method. Run blank on chemicals used in Method 2.

(3) *Modified Volhard*.—Weigh approximately 3 grams of cheese accurately into a 300 cc. Erlenmeyer flask; add more than enough 0.1 *N* silver nitrate solution to combine with all the chlorine; boil the mixture with 10 cc. of halogen-free nitric acid and about 50 cc. of water. Add 5% potassium permanganate solution, 5 cc. at a time, while boiling, until about 15 cc. is added (the solution becomes yellowish and clear). Dilute the solution to about 100 cc., filter the sediment off and thoroughly wash with hot water. Titrate the excess silver nitrate with 0.1 *N* potassium sulfocyanate in the presence of a saturated solution of ferric alum (approximately 5 cc.) as indicator. Run a blank on the chemicals, following the same procedure and using sugar in order to destroy the  $\text{KMnO}_4$ . Calculate the chlorine found and report as sodium chloride.

In Table 1 are given the results obtained by the collaborators on different types of cheese.

The results of the collaborators show that a loss of salt occurs when the present method of ashing cheese is used. It is also clearly shown that enough base to neutralize the acidity must be present, but no indication is given as to what base should be added. In some cases 0.5 gram of base to 2 grams of cheese is sufficient, but when the acidity is high, with a high salt content, loss of salt seems to occur, or this loss may be due to too high a temperature in the ashing.

The modified Volhard method tried by the collaborators seems to give reliable results and it is very rapid; the one disadvantage is that ash and salt cannot be run on the same weighed sample.

The results as a whole on the different cheese samples analyzed show a loss of salt by the present official method for salt in cheese when compared with the other two methods used. The exception is in the case of the two process cheese samples, which had an emulsifier present which acted as a base.

If further work continues to yield the same trend in the ash and salt results the present official method should be revised. It would be desirable to run the salt on the ashed sample but this brings in the question of a blank in order to fix the salt during the ashing. It would then be necessary to determine this correction on each batch of reagents that were used in fixing the salt for the ash determination.

#### RECOMMENDATIONS<sup>1</sup>

It is recommended—

- (1) That the methods for citric and tartaric acids<sup>2</sup> submitted in 1931 be made official, final action.
- (2) That no further work be done on the  $\text{P}_2\text{O}_5$ -CaO ratio.
- (3) That further collaborative work be done on the ash and salt con-

<sup>1</sup> For report of Subcommittee C and action of the Association, see *This Journal*, 17, 57 (1934).

<sup>2</sup> *Methods of Analysis*, A.O.A.C., 1930, 240, 241.

TABLE 1.—Sodium chloride in cheese (different methods)  
Ashing at 550°C.

		WITHOUT ADDED BASE	AVERAGE	WHITE Ca ACETATE	AVERAGE	WITH Na <sub>2</sub> CO <sub>3</sub>	AVERAGE	MODIFIED VOLKARD METHOD	AVERAGE
		per cent	per cent	per cent	per cent	per cent	per cent	per cent	per cent
Frank H. Collins St. Louis	Swiss Process	2.18 2.15	2.17			2.24 2.24		2.29 2.25	2.26
Guy G. Frary Vermillion *	Cheddar Wisconsin	.72 .75 .71	.73	1.26 1.21 1.23				1.31 1.31 1.31	1.31
S. M. Stark Minneapolis	Cheddar Twin Daisy	1.38 1.39	1.39	1.81 1.80	1.81	1.82 1.82	1.82	1.80 1.80	1.80
C. B. Stone	Cheddar Loaf Style	.97 .99	.98	1.33 1.35	1.34	1.33 1.33	1.33	1.32 1.32	1.32
	Cheddar Loaf Style	1.07 1.07	1.07	1.43 1.43	1.43	1.43 1.45	1.44	1.41 1.41	1.41
	Cheddar Longhorn	1.37 1.35	1.36	1.68 1.68	1.68	1.70 1.70	1.70	1.72 1.70	1.71
	Domestic Swiss	.95 .97	.96	1.30 1.32	1.31			1.30 1.30	1.30
	Domestic Swiss	.78 .78	.78			1.20 1.20	1.20	1.18 1.18	1.18
	Process American	1.86 1.87	1.87			1.89 1.89	1.89	1.87 1.87	1.87
	Process Swiss American	1.05 1.08	1.07			1.10 1.10	1.10	1.08 1.10	1.09

\* 600°C.

tent of cheese, the Volhard method to be used and checked against other standard methods.

(4) That the work on added gums in cheese be done by the Referee on Gums in Foods.

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No report on dried milk was given by the associate referee.

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## REPORT ON MALTED MILK

By FRED HILLIG (U. S. Food and Drug Administration,  
Washington, D. C.), *Associate Referee*

Last year the Association approved three recommendations on the subject of malted milk. The first recommendation, relative to the determination of the Reichert-Meissl value of fat obtained by the method of extraction previously proposed, was not acted upon for reasons that will be discussed later. In regard to the second recommendation pertaining to the determination of milk solids by means of citric acid, it was found that malt itself contains appreciable quantities of the acid. Time did not permit consideration of the third recommendation regarding the determination of casein.

In 1931 the Associate Referee submitted for collaborative study two samples of malted milk for the determination of fat by the tentative method. The duplicates reported were in good agreement, but the data submitted by the different analysts were not satisfactory. The results of eleven analysts for the two samples ranged from 8.90 to 9.72 and 8.03 to 8.69 per cent, respectively. The details of this work were not reported. It is apparent that in the hands of different chemists the tentative method is not entirely satisfactory.

After carefully considering the technic of the official Roesse-Gottlieb method the Associate Referee concluded that the difficulties encountered by the various analysts in obtaining concordant results are in all probability due to (1) the small quantity of malted milk used, (2) the occurrence of emulsions, and (3) the inclusion of non-fat material in the extract. In the method here proposed provisions were made to eliminate these difficulties. The main feature in which the proposed method differs from the general methods for the determination of fat lies in the fact that the fat is collected in "filter cel" before extraction. It is not known to whom the credit for the use of filter cel is due; in this Administration it was first applied by V. E. Munsey in the determination of fat in bread. With respect to accuracy and time required the proposed method has no advantages over the Roesse-Gottlieb method. The accuracy of the Roesse-Gottlieb method has been established. However, the details of the deter-

mination must be strictly adhered to, particularly those regarding the purification of the dried fat by petroleum ether. The method proposed gives extractions practically free of non-fat material, making a resolution with petroleum ether unnecessary.

#### PROPOSED METHOD FOR DETERMINATION OF FAT IN MALTED MILK

Weigh accurately into a 250 cc. beaker about 5 grams of the well-mixed sample, add 5 cc. of water, and stir into a smooth paste. Add 10 cc. of strong hydrochloric acid and place the mixture on the steam bath for 30 minutes, stirring frequently. Cool, add 50 cc. of ice-cold water and about 5 grams of "filter cel," and chill in ice water for 30 minutes. Place a close fitting piece of linen into a 2 inch Büchner funnel and carefully overlay with about 1.5 grams of refined infusorial earth ("filter cel" has been found satisfactory). Pour the hydrolyzed mixture into the Büchner funnel and so apply suction that the pad does not pull away from the walls of the funnel. Pour the filtrate back into the beaker and refilter. Rinse the beaker three times with ice-cold water, being careful not to suck the pad too dry. Finally wash the pad three times with ice-cold water and transfer the material to the original beaker. Remove the linen, break up the pad with a flattened stirring rod, place on the steam bath for about 30 minutes to drive off most of the moisture and then in the water oven for about 30 minutes. To the finely powdered material add 15 grams of *anhydrous* sodium sulfate and mix well. Add 50 cc. of ether (previously shaken with anhydrous sodium sulfate) and stir 2 minutes with the flattened stirring rod, breaking up any lumps that may be present. Add 50 cc. of petroleum ether and stir 2 minutes. Decant onto a thick (about  $\frac{1}{2}$  inch) tightly tamped pad of asbestos in a large Knorr tube and transfer the residue to the tube. (The Knorr tube may be made from a discarded 200 cc. pipet.) Filter into a tared flask. Suck as dry as possible, using the flattened stirring rod to tamp the material in the Knorr tube. Rinse the beaker with 50 cc. of the mixed ethers (1 to 1), pour into the tube, stir until the ethers are well mixed with the material, and allow to stand several minutes. Suck dry, tamping the material as before, and make four additional extractions in the same manner. Evaporate the ethers and dry in a water oven to constant weight.

The results show that when applied to malted milk the tentative and the proposed methods give well agreeing results. It is noted, however, that with the exception of Sample 4 the average results by the tentative method are slightly higher than those by the proposed method. This may be due to the incomplete removal of non-fat material; the average non-fat material for the eleven determinations was 1.3 mg., and the range from 0.4 to 2.7 mg.

For the determination of the Reichert-Meissl value it is imperative that the fat used be representative of the entire fat content of the material. So far as the writer is aware the literature does not give a uniform procedure for fat isolation. Preliminary work convinces the Associate Referee that the method of extraction outlined yields a fat that is representative of the fat content of malted milk, and that the procedure can be adjusted to obtain the 5 grams of fat required for the Reichert-Meissl value by using a larger quantity of the material.

C. W. Ballard, City of New York Department of Health, suggests

*Comparative results obtained by the tentative and proposed methods*

SAMPLE	FAT DETERMINED BY—			
	TENTATIVE METHOD		PROPOSED METHOD	
	<i>per cent</i>		<i>per cent</i>	
1	7.80		7.84	
	7.81	7.81	7.72	
			7.75	
			7.74	7.76
2	9.14		9.15	
	9.16	9.15	9.13	
			9.07	9.12
3	8.83		8.74	
	8.87		8.68	
	8.80	8.83	8.64	8.70
4	8.55		8.68	
	8.61	8.58	8.62	
			8.70	8.67
5	7.96		7.89	
	7.91	7.94	7.81	
			7.84	7.85

that for the mounting of malted milk preparations for microscopic identification, a mixture of glycerin, alcohol, and water (1:1:1) be used. He believes that by using such a mixture instead of oil for mounting better detail in this work is possible.

RECOMMENDATIONS<sup>1</sup>

It is recommended—

(1) That no further work be undertaken on the determination of the Reichert-Meissl value by the method previously proposed.

(2) That study of the determination of milk solids through a citric acid determination be dropped.

(3) That last year's recommendation for the determination of casein be carried over.

(4) That the determination of fat by the method proposed be studied collaboratively and that further work be done on the determination of the Reichert-Meissl value on fat so extracted.

(5) That the type of mounting suggested by Ballard be studied.

<sup>1</sup> For report of Subcommittee C and action of the Association, see *This Journal*, 17, 56 (1934).

## REPORT ON ICE CREAM

By GUY G. FRARY (State Chemical Laboratory, Vermillion, S.D.),  
*Associate Referee*

The Associate Referee on Ice Cream studied various modifications of the Babcock test as applied to this product. Excellent cooperation was received from a number of laboratories and to these collaborators the Associate Referee wishes to express his appreciation. In addition to the two methods recommended for study last year, each collaborator was asked to work with the method used in his laboratory for routine examinations. Thus a variety of modifications of the Babcock test was tried.

The subject under investigation is an old one, and it has been studied rather thoroughly in the past. In 1915, Hortvet<sup>1</sup> reviewed the previous work of the Association on the subject of fat in dairy products as far back as 1906 and reported in details work done during the year under his direction as associate referee. In his instructions to collaborators Hortvet then said, "There is an urgent call for a reliable centrifugal method for condensed milk and ice cream, and it is hoped that the collaborative work of the present (1915) season will bring about some agreement, at least on essential points, in connection with one or more of the methods which have been proposed." Two of the three centrifugal methods studied that year specified sulfuric and acetic acids; they were designated the Brinsmaid and the Grigsby methods. A third method, the Wendler, employed an alkaline solution of Rochelle salt and sodium chloride. The Roese-Gottlieb method, which up to that time had been adopted only provisionally for some dairy products, was also studied. In addition to ice cream, whole milk, sweet cream and evaporated milk were studied. The Referee asked that the Roese-Gottlieb, Wendler, and Grigsby methods be used for ice cream. Although not yet adopted as official, the first of these had been thoroughly tried over a period of years and had been proved to be reliable. Of the many modifications of the Babcock test which had been suggested, Hortvet remarked as follows: "The supply of such methods in the last half-dozen years has perhaps much exceeded the demand; most of them have gone into print without anything like adequate analytical backing, and the originators have been for the most part over-confident and somewhat lax in their descriptions." The results obtained by the collaborators with the Wendler and Grigsby methods were not satisfactory, the former giving notably poor fat columns. Referee Hortvet recommended further study of modifications of the Babcock method as applied to ice cream.

Results obtained by collaborators in 1916 were not favorable to any of the modifications of the Babcock method, and the Referee fails that year to recommend further study of such methods. He did, however,

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<sup>1</sup> *This Journal*, 4, 238 (1917).



favor further study of the Roesse-Gottlieb method as applied to plain ice cream, and in 1917 recommended its adoption as official. No further work on the application of the Babcock method to ice cream seems to have been reported by Hortvet and he does not refer again to such methods until 1923,<sup>1</sup> when he makes the following statement: "A number of years ago, while the writer was serving as referee on this group of products, collaborative work covering three years resulted in the decision that no modification of the Babcock test is reliable when applied to cheese, condensed and evaporated milk and ice cream. So far as the actual status of these modifications is concerned, in this Association they are now in the refuse class."

Despite the adverse findings of Referee Hortvet there has remained in use a variety of methods for fat in ice cream which are based on the Babcock test. Many regulatory laboratories use these methods for sorting samples and then confirm results on those that appear to be questionable by using the official method. A number of requests have been received for a method recognized by this Association, and it has been suggested that there might be found some modification that would give results sufficiently accurate to permit its adoption as tentative. However, the Referee has thought that none of these centrifugal methods is exact enough to justify its recommendation as an official method.

A thorough study of the problem made by Crowe at the University of Nebraska Experiment Station in 1930<sup>2</sup> developed a method which the author proposed as satisfactory "for almost any commercial purpose." The test was "not presented as a replacement of ether extraction methods, but only as a procedure to be used where such methods are not available, or as a test preliminary to such procedure." The consistent results reported by Crowe led the Referee last year to recommend that collaborative study of the method be made, especially because it appeared to give equally good results with chocolate, fruit ice creams and plain ice cream.

In 1930, Overman and Garrett, working at the Illinois Experiment Station, reported their study of modifications of the Babcock test applicable to ice creams.<sup>3</sup> They reviewed the literature on the subject and then attempted to find an alkaline reagent suitable for use in the Babcock apparatus. They prepared and tried 261 different solutions and studied the effect of ten different organic compounds in conjunction with the solutions. A strong solution of tri-sodium phosphate and sodium acetate, used with an ammoniacal solution of *n*-butyl alcohol and ethyl alcohol, gave best results. Their work lead them to conclude that "butterfat can be separated quantitatively from ice cream without the use of sulfuric acid," and that "the method presented is fairly rapid, sufficiently accurate for commercial use, and is inexpensive." This modification, like that pro-

<sup>1</sup> *This Journal*, 8, 6 (1924).

<sup>2</sup> Univ. Nebraska Exp. Sta. Bull. 246 (1930).

<sup>3</sup> Univ. Illinois Exp. Sta., Bull. 360 (1930).

*Butterfat in ice cream (per cent) by modified Babcock methods*

COLLABORATOR	KIND	NEBRASKA METHOD					ILLINOIS METHOD					OPTIONAL METHOD				
		AVERAGE VARIATION					AVERAGE VARIATION					AVERAGE VARIATION				
		BELOW OFF. METHOD	ABOVE OFF. METHOD	ALL SAMPLES	BELOW OFF. METHOD	ABOVE OFF. METHOD	BELOW OFF. METHOD	ABOVE OFF. METHOD	ALL SAMPLES	BELOW OFF. METHOD	ABOVE OFF. METHOD	BELOW OFF. METHOD	ABOVE OFF. METHOD	ALL SAMPLES	BELOW OFF. METHOD	ABOVE OFF. METHOD
W. C. Jones Dept. of Agriculture Virginia	Vanilla Chocolate Misc.	(2)*0.36 (5) 0.24	(2) 0.08 (1) 0.52 (3) 0.39	0.22 0.52 0.30		(3) 0.92 (1) 2.02 (6) 0.77	(3) 0.26	(3) 0.92 (1) 2.02 (6) 0.77	(4) 0.69 2.02 0.64	(1) 0.77	(3) 0.96 (1) 0.39 (8) 0.89	(1) 0.77	(3) 0.96 (1) 0.39 (8) 0.89	0.66 0.39 0.89		
N. E. Yongue District Health Dept. Washington, D. C.	Vanilla Chocolate Misc.	(6) 0.46 (9) 0.77 (1) 1.40	(6) 0.36 (2) 0.35	(13) 0.38 0.69 1.40	(3) 0.20 (6) 0.27 (1) 0.40	(9) 1.13 (3) 1.16		(9) 1.13 (3) 1.16	0.94 0.57 0.40							
E. R. Redfern Dept. of Agriculture Iowa	Vanilla Chocolate Misc.	(1) 1.10 (2) 2.13 (1) 1.32		1.10 2.13 1.32	(1) 0.50 (2) 1.83 (1) 0.92				0.50 1.83 0.92	(1) 0.10	(1) 0.30 (1) 0.85 (1) 0.68	(1) 0.10	(1) 0.30 (1) 0.85 (1) 0.68	0.30 0.48 0.68		
C. S. Ladd & H. W. Conroy Regulatory Dept. North Dakota	Vanilla Fruit Nut	(5) 0.27 (2) 0.38 (1) 0.16		0.27 0.38 0.16	(2) 0.21 (2) 0.29 (1) 0.21	(3) 0.27		(3) 0.27	0.25 0.29 0.21							
Henry Hoffman, Jr. Dept. of Agriculture Minnesota	Vanilla Fruit Nut			(1) 0.00 (1) 0.00 0.13		(1) 0.80 (1) 0.69 (1) 0.73		(1) 0.80 (1) 0.69 (1) 0.73	0.80 0.69 0.73		(1) 0.55 (1) 0.74 (1) 0.78		(1) 0.55 (1) 0.74 (1) 0.78	0.55 0.74 0.78		
J. T. Keister Food & Drug Adm. Washington, D. C.	Vanilla Chocolate Fruit	(2) 0.20 (2) 1.03 (4) 1.00	(1) 0.28	0.23 1.03 1.00	(1) 1.27	(3) 0.79 (1) 0.00 (4) 0.87	(1) 3.70 (3) 4.37	(3) 0.79 (1) 0.00 (4) 0.87	0.79 0.63 0.87	(1) 0.39 (3) 0.53	(2) 0.14	(1) 0.39 (3) 0.53	(2) 0.14	0.14 0.39 0.53		
Horatio N. Parker Health Department Jacksonville, Florida	Vanilla Chocolate	(1) 3.20 (3) 0.80	(4) 1.70 (1) 0.40	2.10 (5) 0.56	(1) 3.70 (3) 4.37	(4) 0.70 (1) 0.30		(4) 0.70 (1) 0.30	1.50 (5) 2.68	(2) 2.85	(3) 1.02	(2) 2.85	(3) 1.02	1.75		
C. D. Howard & H. I. Albee State Board of Health New Hampshire	Vanilla Fruit Misc.†	(6) 0.21 (1) 0.19 (2) 0.17		0.21 0.19 0.17	(1) 0.15	(5) 0.16 (1) 0.31 (2) 0.08		(5) 0.16 (1) 0.31 (2) 0.08	0.16 0.31 0.08	(6) 0.24 (1) 0.19 (2) 0.17		(6) 0.24 (1) 0.19 (2) 0.17		0.24 0.19 0.17		
G. G. Frary & R. Adams State Chemical Lab. South Dakota	Vanilla Chocolate Misc.	(14) 0.66 (3) 1.43 (2) 0.35	(2) 1.83	0.66 1.79 0.35	(2) 0.48 (4) 1.93 (1) 0.06	(9) 0.23		(9) 0.23	(13) 0.23 1.93 .51	(2) 0.08 (5) 0.86 (2) 0.47	(10) 0.23	(2) 0.08 (5) 0.86 (2) 0.47	(10) 0.23	(14) 0.18 0.86 0.47		

\* Numbers in parentheses indicate the number of samples tested.

posed by the Nebraska workers, gave equally good results with chocolate, fruit and plain ice creams.

Nine collaborators assisted in the study this year. They were instructed to make tests on as many samples as time would permit, to use a variety of ice creams, and to run all samples by the official method and by the two proposed methods. If possible, the samples were also to be tested by any modification of the Babcock method used by the collaborator for routine examinations. As the details of the methods and of preparations of the necessary solutions are rather voluminous, they are not given here. They were essentially those printed in the "Laboratory Manual" compiled and published in 1933 by the International Association of Milk Dealers.

A summary of the results obtained is given in the table. The following collaborators reported results by a third modification of the Babcock test.

W. C. Jones, Virginia, (Bradbury method).<sup>1</sup>

E. L. Redfern, Iowa, (method specifying ammonia, butyl alcohol and sulfuric acid).<sup>2</sup>

Henry Hoffman, Minnesota, and C. D. Howard, New Hampshire, (Lichtenberg method).<sup>3</sup>

J. T. Keister, Washington, D. C., (Grigsby method).<sup>4</sup>

H. N. Parker, Jacksonville, Fla., (Doan test, another modification specifying acetic and sulfuric acids).

The Referee used still another modification specifying acetic and sulfuric acids, and it is thus seen that of the optional methods used by collaborators in addition to the two methods sent out by the Referee five of the seven specify acetic and sulfuric acids.

The results obtained are not encouraging, only a very few being near the actual fat content as shown by the official method. The variations in some cases are enormous and not easily explained. Doubtless lack of familiarity with the methods accounts for some error. The authors of the methods state that operators must become "completely familiar" with the methods in order to achieve success with them. Difficulty in reading fat columns because of char and curd may partially explain the poor showing. Comments by the collaborators are of interest and shed some light, as follows:

#### COMMENTS OF COLLABORATORS

*W. Catesby Jones.*—Separation by Nebraska method indistinct and char bad. Illinois method, clear separation, no char, some curd.

*N. E. Yongue.*—Nebraska method gives char below lower meniscus in most cases, too much in one case for reading on a chocolate ice cream. With vanilla creams the separation was usually good. The Illinois method gave better fat columns but in some cases reagent alcohol was found in the separated fat, accounting, in part at least, for high results.

<sup>1</sup> Virginia Dairy and Food Div., Circ. 42 (1914).

<sup>2</sup> Pennsylvania Exp. Sta., Bull. 258 (1930).

<sup>3</sup> Leach, *Food Inspection and Analysis*, 4th Ed., p. 195.

<sup>4</sup> Illinois Dairy and Food Com. Bull. 28.

*E. L. Redfern.*—Nebraska method gives slug under fat column in each case and the Illinois method in one sample. Other fat columns clear. Penn State method gives clear fat columns free in nearly every case from any slug under the fat.

*C. S. Ladd.*—Base of the fat column not very clear in Nebraska test. Fats were clear. Trouble seems to be in securing a definite lower meniscus. Fresh reagents improve Nebraska test.

*Henry Hoffman.*—Fat column very good, clear and free from any char, making it very accurate to read in Nebraska method. Illinois method, fat column very good, no charring whatever. Lichtenberg method shows slight charring in some cases. Care must be taken in adding the sulfuric acid.

*J. T. Keister.*—Some char at bottom of fat with vanilla as well as with fruit and chocolate ice creams in both Nebraska and Illinois tests, but char separated from fat in Illinois test, making fat reading good.

*H. N. Parker.*—The Nebraska method gave clear fat readings and is convenient. Illinois method gives beautifully clear butterfats and I . . . believe if the operator becomes practiced with it the method will prove accurate and cheap.

*C. D. Howard.*—Nebraska method: easy manipulation, column clear, only slight charring or debris regardless of flavor of ice cream. Illinois method: manipulation tricky. Several portions lost by frothing over during shaking in water bath. Fat percentage consistently high. Column clear with no debris or charring. If bottles were allowed to remain without shaking until all visible frothing had disappeared loss did not occur. Neither method is so simple or rapid as the Lichtenberg method, although fat columns are more satisfactory.

It is the opinion of the Referee that at least another year should be allowed for study of modifications of the Babcock method for fat in ice creams. It is the experience of the Referee and of at least one collaborator that the reagents for the Nebraska test must be fresh for best results, and that in the Illinois test care must be taken during heating of the samples to avoid loss.

It is recommended<sup>1</sup> that the study of modifications of the Babcock centrifugal method for fat as applied to ice cream be continued.

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## REPORT ON MILK PROTEINS

By MARIE L. OFFUTT (U. S. Food and Drug Administration,  
New York, N. Y.), *Associate Referee*

Last year the collaborators were requested to try out the tentative A.O.A.C. method for casein and a proposed method for albumin.<sup>2</sup> Only two collaborators sent in results. The same methods with a slight variation in the proposed method for albumin were sent this year.

The results obtained by the collaborators are given in the table.

It is recommended<sup>1</sup> that the proposed method for casein be adopted

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<sup>1</sup> For report of Subcommittee C and action of the Association, see *This Journal*, 17, 57 (1934).

<sup>2</sup> *This Journal*, 16, 490 (1933).

*Casein (grams per 100 cc.)*

SAMPLE	COLLABORATOR	TOTAL PROTEIN (N×6.38)	OFFICIAL METHOD	TENTATIVE METHOD	DIFFERENCE
1	J. T. Keister	3.36; 3.27 Av. 3.32	2.46; 2.46 Av. 2.46	2.54; 2.53 Av. 2.54	+0.08
2		3.59; 3.59 Av. 3.59	2.68; 2.72 Av. 2.70	2.79; 2.81 Av. 2.80	+0.10
3		3.42; 3.44 Av. 3.43	2.55; 2.55 Av. 2.55	2.63; 2.63 Av. 2.63	+0.08
1	M. L. Offutt	3.14	2.59	2.58	-0.01
2		3.16	2.43	2.59	+0.16
3		3.11	2.32	2.47	+0.15
1	R. L. Vandaveer	3.96; 3.97 Av. 3.97	2.95; 2.93 Av. 2.94	3.09; 3.08 Av. 3.09	+0.15
2		3.91; 3.92 Av. 3.92	2.86; 2.89 Av. 2.88	2.97; 2.98 Av. 2.98	+0.10
3		3.94; 3.87 Av. 3.91	2.97; 2.98 Av. 2.98	3.06; 3.06 Av. 3.06	+0.08

*Albumin (grams per 100 cc.)*

SAMPLE	COLLABORATOR	OFFICIAL METHOD	PROPOSED METHOD	DIFFERENCE
1	J. T. Keister	0.45; 0.43 Av. 0.44	0.39; 0.43 Av. 0.41	-0.03
2		0.52; 0.52 Av. 0.52	0.41; 0.36 Av. 0.39	-0.13
3		0.44; 0.47 Av. 0.45	0.45; 0.43 Av. 0.44	-0.01
1	M. L. Offutt	0.22	0.27	+0.05
2		0.30	0.35	+0.05
3		0.34	0.44	+0.10
1	R. L. Vandaveer	0.47; 0.48 Av. 0.48	0.57; 0.57 Av. 0.57	+0.09
2		0.50; 0.50 Av. 0.50	0.44; 0.40 Av. 0.42	-0.08
3		0.43; 0.44 Av. 0.44	0.50; 0.50 Av. 0.50	+0.06

as official (first reading) and that the revised proposed method for albumin be adopted as tentative.

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No report on naval stores was given by the referee.

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No report on turpentine was given by the associate referee.

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No report on paints, paint materials, and varnishes was given by the referee.

## TUESDAY—AFTERNOON SESSION

At the opening of the afternoon session, Dr. P. A. Webber, Madison, Tenn., gave an illustrated lecture on the soy bean.

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No report on beers, wines, and distilled liquors was given by the referee.

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### REPORT ON VINEGARS

By A. M. HENRY (U. S. Food and Drug Administration,  
Philadelphia, Pa.), *Referee*

#### GLYCEROL

Studies reported for two years have shown that diphenylamine as an inside indicator is preferable to potassium ferricyanide as an outside indicator.

Collaborators were requested to determine the glycerol of any vinegars they were analyzing by both the official method and the proposed modification, and to use diphenylamine as indicator [*This Journal*, 15, 536 (1932)].

The results obtained by the collaborators are given in Table 1.

#### COMMENTS BY COLLABORATORS

*S. Alfend.*—As in previous work, I found the inside indicator titration preferable to the present official method.

*M. J. Gnagy.*—The titration with diphenylamine is much preferred over the titration with an outside indicator. The end point on the first titration with diphenylamine was missed, but no trouble was encountered when the titration was made in a better light.

*A. K. Klein.*—I am very enthusiastic over the new method proposed for titrating glycerine solutions with the inside indicator. Titrations are more easily and more certainly reproducible, and the manipulation of the titration requires only the ordinary titrating experience. The older method, however, using the outside potassium ferricyanide indicator requires judgment and experience. It is much more tedious and painstaking, and its results are never so certain as those of the method specifying the inside indicator.

*W. L. Scovill.*—Duplicate portions of the sample of vinegar were carried through the oxidation with the dichromate and several titrations were made on each. The glycerol is reported to the third decimal place to show the small differences in the various titrations. Results obtained by this method are practically the same as with the outside indicator. After using this method a few times the analyst would probably prefer it to the present method.

In view of the close agreement of the collaborators on samples of glycerol last year, and on various vinegars this year by the two methods, the adoption of the new method with the more convenient inside indicator, is recommended.

TABLE 1.—*Collaborative results (glycerol)*

COLLABORATOR	SAMPLE NUMBER	GRAMS GLYCEROL PER 100 CC. VINEGAR	
		OFFICIAL METHOD POTASSIUM FERRI- CYANIDE INDICATOR	PROPOSED METHOD DIPHENYLAMINE INDICATOR
S. Alfend	1	0.265	0.265
		0.265	0.265
	2	0.272	0.272
		0.270	0.272
S. L. Crawford	1	0.192	0.198
	2	0.168	0.174
M. J. Gnagy	1	0.304	0.304
		0.307	0.307
A. K. Klein	1	0.246	0.249
	2	0.281	0.286
A. H. Robertson	1	0.202	0.206
	2	0.256	0.257
	3	0.186	0.182
	4	0.191	0.188
	5	0.331	0.331
	6	0.276	0.275
W. L. Scovill	1	0.174	0.176
		0.176	0.177
	2	0.178	0.172
		0.176	0.174
		0.175	0.173
Average of 15 samples		0.242	0.244

## TOTAL SOLUBLE ASH AND PHOSPHORIC ACID

H. Shuman, Food and Drug Administration, Philadelphia, Pa., has continued investigation on these subjects, but has not finished the work.

## SOLIDS

Study of the occlusion of acetic acid by the solids during evaporation, when determining solids, was continued. Previous results tend to confirm Laudig's original contention [*This Journal*, 10, 520 (1927)] that relative humidity and air pressure may be contributing factors. It is also possible that rate of evaporation and other factors governing the film formation on the surface of the drying vinegar are important in this connection.

In order to obtain data as to how prevalent the retention of acetic is when only one evaporation is made, collaborators were requested to make



TABLE 2.—*Collaborative results (solids)*

COLLABORATOR	GRAMS SOLIDS PER 100 CC. OF VINEGAR		
	TENTATIVE METHOD	LAUDIG'S MODIFICATION	LOSS
S. Alfend	1.66	1.63	.03
S. L. Crawford	2.57	2.50	.07
	2.56	2.49	.07
	2.12	2.02	.10
	2.05	1.96	.09
	2.14	1.96	.08
	2.03	1.92	.11
	1.87	1.81	.06
	1.56	1.52	.04
	1.34	1.31	.03
	2.16	2.05	.11
	2.48	2.36	.12
	2.19	2.12	.07
	2.49	2.40	.09
M. J. Gnagy	1.32	1.26	.06
	1.34	1.27	.07
A. K. Klein	1.97	1.88	.09
	2.00	1.87	.13
J. F. Laudig (Cider vinegar)	1.10	1.07	.03
	1.10	0.56	.54
	1.13	0.95	.18
	1.03	0.95	.08
	0.97	0.90	.07
	0.99	0.55	.44
	0.94	0.89	.05
	0.93	0.86	.07
	0.90	0.86	.04
	0.90	0.89	.01
	0.99	0.93	.06
	0.90	0.88	.02
	1.46	1.45	.01
	1.16	1.16	.00
	1.21	1.16	.05
	1.22	1.14	.08
	1.40	1.32	.08
	1.28	1.21	.07
	1.60	1.49	.11
	1.74	1.60	.14
	1.22	1.17	.05
	1.41	1.16	.25
	1.25	1.14	.11
	1.27	1.20	.07
	1.52	1.30	.22
	1.33	1.23	.10
	1.33	1.26	.07
	1.36	1.29	.07
	1.54	1.48	.06
	1.66	1.59	.07
	1.27	1.25	.02
	1.34	1.31	.03

COLLABORATOR	GRAMS SOLIDS PER 100 CC. OF VINEGAR		
	TENTATIVE METHOD	LAUDIG'S MODIFICATION	LOSS
	1.67	1.61	.06
	1.48	1.42	.06
(Malt vinegar)	3.15	2.42	.73
	3.72	3.35	.37
	3.03	2.76	.27
	3.26	2.22	1.06
	2.67	2.45	.22
	2.73	2.50	.23
	3.12	2.30	.82
	2.84	2.54	.30
	2.61	2.37	.24
	2.64	2.31	.33
	2.73	2.36	.37
	2.44	2.10	.34
	2.38	2.10	.28
	2.87	2.49	.38
	2.91	2.36	.55
	2.44	2.19	.25
	2.96	2.74	.22
	2.50	2.30	.20
	2.67	2.56	.11
	2.85	2.68	.17
	2.56	2.46	.10
	2.88	2.49	.39
	2.51	2.40	.11
(Sugar vinegar)	0.63	0.60	.03
	0.87	0.81	.06
	0.80	0.73	.07
	0.72	0.69	.03
	0.70	0.70	.00
	1.24	1.21	.03
	1.32	1.22	.10
	1.31	1.19	.12
	1.31	1.23	.08
A. H. Robertson	(a) 1.69	1.65	.04
	1.69	1.62	.07
	(b) 3.28	3.22	.06
	3.26	3.17	.09
	3.28	3.28	.00
	3.29	3.27	.02
	(c) 1.31	1.27	.04
	1.32	1.30	.02
	(d) 2.68	2.65	.03
	2.69	2.61	.08
	(e) 2.74	2.68	.06
	2.73	2.67	.06
W. L. Scovill	2.87	2.67	9.20
	2.83	2.70	9.13
	2.80	2.67	.13

determinations of solids on any samples of vinegar they were analyzing by the tentative method and by Laudig's modification.

The results obtained by the collaborators are given in Table 2.

The only collaborator that found any great variation in the two methods was J. F. Laudig, who made 66 of the 88 determinations reported. All the determinations were made between January 1st and April 30th. Consequently the high relative humidities present at times in summer were not a factor.

The collaborators were also asked, after drying the solids for exactly 2.5 hours and weighing, to again dry for an hour and weigh. Results submitted show the effect of this additional drying to be negligible and consequently they are not reported.

The solids on some vinegar (cider) as well as on malt, decrease when water is added and again evaporated. Further work is necessary to develop a satisfactory method.

#### RECOMMENDATIONS<sup>1</sup>

It is recommended—

(1) That the methods for the determination of total and soluble ash be further studied, with particular attention given to the use of sucrose or other substances for reducing the time of heating and to the temperature of ashing.

(2) That the methods for the determination of phosphoric acid be further studied in connection with the studies on ash.

(3) That the official method for the determination of solids be studied, especially with reference to its application to vinegar high in solids, such as malt vinegar.

(4) That the proposed change [*This Journal*, 15, 536 (1932)] in the glycerol method, be adopted as official (first action). It includes the substitution of diphenylamine as an inside indicator for potassium ferricyanide as an outside indicator, and the simplified method of calculating glycerol.

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#### REPORT ON FLAVORS AND NON-ALCOHOLIC BEVERAGES

By JOHN B. WILSON (U. S. Food and Drug Administration,  
Washington, D. C.), *Referee*

The Referee continued work on the two methods for the determination of essential oil in extracts and toilet preparations that were studied collaboratively last year. Oil was determined in the samples sent out last year, and the results obtained by the Referee are given in Table 1. These results cause little if any change in the averages obtained by collabora-

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<sup>1</sup> For report of Subcommittee C and action of the Association, see *This Journal*, 17, 60 (1934).

tors reporting last year. The discrepancies in the case of extracts of peppermint and spearmint were further studied by the Referee. The peppermint oil was made up into several extracts of different strengths, and several other peppermint oils were made into extracts of standard strength and analyzed by Method I.

TABLE 1.—*Determination of essential oil\* (per cent)*

EXTRACT	OIL PRESENT	OIL FOUND	
		Method I	
Anise	3.5	3.5	3.6
Lemon	5.0	5.0	4.9
Nutmeg	2.0	2.0	2.1
Orange	5.0	5.0	4.7
Peppermint	3.0	3.4	3.3
Rose	1.0	0.5	0.4
Rosemary	2.0	2.0	1.9
Spearmint	3.0	2.8	2.7
Thyme	0.5	0.6	0.6
Imitation Wintergreen	3.0	3.0	3.0
		Method II	
Cinnamon	2.5	2.5	2.4
Clove	2.5	2.5	2.6

\* Results obtained by the Referee on samples examined by collaborators last year [*This Journal*, 16, 542 (1933)].

Since results as high as those of last year were obtained, the data furnished the Referee by the Bureau of Industrial Alcohol were consulted, and it was found that these were also high (3.4 per cent found in each of the five instances reported when 3.0 per cent of peppermint oil was present). The same extracts were treated by Method II, which gave low results. Method II was modified by the substitution of saturated sodium chloride solution for magnesium sulfate solution, which likewise gave low results. Method I, modified by substituting a saturated calcium chloride solution for sodium chloride solution was applied to the peppermint extracts. These results are very encouraging, and the Referee believes this procedure should be studied collaboratively. The results obtained by the above procedures are given in Table 2.

Several of the procedures mentioned were applied to spearmint extracts and yielded the results given in Table 3, none of which is considered acceptable. It may be possible, however, to use Method I in conjunction with the factor 1.11 since the results obtained so far by this method appear to have about that relation to the quantity of oil present.

It is recommended<sup>1</sup> that methods for determination of essential oil in extracts and toilet preparations be studied collaboratively.

<sup>1</sup> For report of Subcommittee C and action of the Association, see *This Journal*, 17, 60 (1934).

TABLE 2.—*Oil in peppermint extracts (per cent)*

METHOD USED	OIL PRESENT DESIGNATION		OIL FOUND		
I	a	2	2.2	2.2	
	a	3	3.5	3.4	
	a	4	4.6	4.6	
	a	5	5.8	6.0	
	b	3	3.4		
	c	3	3.3		
	d	3	3.3		
	e	3	3.3		
	f	3	2.9		
II					
Floated on saturated $\text{MgSO}_4$	a	2	1.6		
	a	3	2.2		
	a	4	3.5		
	a	5	4.4		
II					
Floated on saturated $\text{NaCl}$	a	2	1.9	1.6	
	a	3	2.6	2.4	
	a	4	3.8	3.8	
	a	5	4.5	4.2	
I					
Floated on saturated $\text{CaCl}_2$	a	2	2.0	1.9	2.0
	a	3	3.0	3.0	3.0
	a	4	4.2	4.2	4.2
	b	3	2.9		
	c	3	2.9		
	d	3	3.0		
	f	3	2.6		

TABLE 3.—*Oil in spearmint extracts (per cent)*

METHOD USED	OIL PRESENT DESIGNATION		OIL FOUND	
I	a	2	1.8	1.8
	a	3	2.7	2.4
	a	3	2.6	2.8
	a	4	3.6	3.6
	a	5	4.8	4.8
	b	3	2.3	2.3
	c	3	2.2	2.2
	d	3	2.4	2.4
II				
Floated on saturated $\text{NaCl}$	a	3	2.5	2.6
I				
Floated on saturated $\text{CaCl}_2$	b	3	2.2	
	c		2.2	
	d		2.2	

## REPORT ON MEAT AND MEAT PRODUCTS

By R. H. KERR (Bureau of Animal Industry,  
Washington, D. C.), *Referee*

Attention was given to methods for determining nitrates and nitrites in meat and in curing solutions. Although a strict interpretation might place the determination of nitrates and nitrites in curing solutions outside the proper field of the Referee on Meat and Meat Products, this problem is so intimately connected with that of determining these substances in meat and in meat extracts that it is hardly possible to consider one without considering the other. The Referee, therefore, considered curing solutions, both used and unused, as well as meat and meat extracts. The laboratory work, most of which is being done by W. C. McVey of the Bureau of Animal Industry, has not yet advanced to the point of sending out samples for collaborative work. It is hoped that the investigation will have progressed sufficiently far next year to make it possible to send out at least one improved method for nitrite nitrogen and one improved method for nitrate nitrogen for collaborative study during the coming year.

It is recommended<sup>1</sup>—

(1) That the study of methods for the determination of nitrate and nitrite nitrogen in meat and meat products, including meat extracts and curing solutions, be continued.

(2) That the method for the determination of salt in meat, presented last year and adopted as tentative, be made official, first action.

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No report on separation of meat proteins was given by the associate referee.

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## REPORT ON GELATIN

By R. M. MEHURIN (Bureau of Animal Industry,  
Washington, D. C.), *Referee*

In conformity with the recommendations made last year, collaborative work was undertaken to determine the most suitable method for preparation of the sample.

Three methods were considered: the tentative (acid hydrolysis), the ashing, and a sulfuric acid digestion method devised by the Referee. A brief description of each method follows:

(1) The tentative method specifies digestion of the gelatin in dilute hydrochloric acid, making the solution slightly alkaline with ammonium

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<sup>1</sup> For report of Subcommittee C and action of the Association, see *This Journal*, 17, 60 (1934).

hydroxide, and precipitating the copper and zinc with hydrogen sulfide, using magnesium ammonium phosphate as an aid in filtering the somewhat viscous solution. This procedure requires about two hours. The method has been criticized for inconsistency of results and slowness of filtration, and doubt has been expressed as to complete precipitation of copper from the hydrolyzed solution by hydrogen sulfide.<sup>1</sup>

(2) The ashing method specifies ignition of the sample without preliminary treatment in a muffle furnace at a temperature of approximately 550°C., which temperature must not be exceeded at any time during the ignition. Complete ashing is essential as is also prevention of overheating and contamination of the ash by particles from a defective furnace. About four hours is required to ash satisfactorily 70 grams of gelatin. Of the three methods described, the Referee has found this one the easiest to follow, and although it is possible that a very small quantity of copper may be lost in the ashing process, it appears to yield, in the hands of collaborators, consistent and reasonably accurate results.

(3) The sulfuric acid digestion method requires digestion of 40 grams of gelatin in an 800 cc. Kjeldahl flask with 180 cc. of concentrated sulfuric acid, without the addition of a catalyst or other oxidizing agent. The digestion is carried out for a preliminary period of 45 minutes over a 3 minute flame (a flame or electric device that heats 100 cc. of distilled water in an 800 cc. Kjeldahl flask from 25°–30° to active boiling in approximately 3 minutes). The heat is then increased to that of a 1½–1½ minute flame, and digestion is continued until the solution is clear. If this degree of heat and the quantities of acid and gelatin are closely adhered to, the digestion will require no further attention and will clear up in 1½–2 hours. If, however, the intensity of heat is decreased or the proportion of acid is increased, the time required for the digestion will be greatly extended; if the reverse of these conditions obtains then the contents of the flask will boil over or will go dry before completion of the digestion. This method requires considerably less time than does the ashing method and it also eliminates the possible aforementioned sources of error inherent in the ashing method. Theoretically this procedure should yield the best results, but the few collaborative reports received indicate that this is not the case. The method should be investigated further before it is recommended.

The sample sent to collaborators was taken from a well-mixed lot of gelatin secured from various sources. Each 40 gram sample contained approximately 0.10 mg. of copper, as determined by various methods, and each collaborator added, before beginning the analysis, 1.27 mg. of copper, making the total amount approximately 1.37 mg. This was done in order to bring the total amount within the range for which the tentative

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<sup>1</sup> *This Journal*, 8, 166 (1924); 9, 458 (1926); 12, 416 (1929).

method for copper in foods has been shown by collaborative tests during the past few years to be reliable. All copper determinations were made by this method in order to secure comparable results.

The samples were sent to eight collaborators, but only four replies were received. Their results and comments follow:

ANALYST	GELATIN	COPPER FOUND BY—		
		TENTATIVE METHOD FOR GELATIN	ASHING METHOD	SULFURIC ACID DIGESTION METHOD
	grams	mg.	mg.	mg.
Kroger Food Foundation	40	0.35	1.33	0.38
Cincinnati, O.	40	0.38	1.29	0.43
J. L. Perlman	40	1.18	1.43	1.53
N. Y. State Dept. of Agr. & Markets	40	1.22	1.43	1.49
Albany, N. Y.				
J. H. Loughrey	40	1.22	—	1.09
U. S. Food & Drug Adm.	40	1.25	—	1.04
New York, N. Y.				
Armour & Co.	40	1.30	1.24	1.20
Chicago, Ill.	40	1.20	1.27	1.33

#### COMMENTS BY COLLABORATORS

*Kroger Food Foundation.—Acid Hydrolysis Method:* While a good sulfide precipitate was obtained with hydrogen sulfide, subsequent ashing of this precipitate after removal of zinc and iron sulfides,  $\text{MgNH}_4\text{PO}_4$ , etc., gave an ash which did not dissolve completely in dilute  $\text{HNO}_3$ . Instead, a considerable amount of a red brown residue remained.

*Ashing Method:* Sodium thiosulfate yielded a good sulfide precipitate which coagulated quickly and which filtered and washed very well. The ash obtained from this residue dissolved readily in the dilute nitric acid.

*Sulfuric Acid Digestion Method:* The copper sulfide precipitate and the free sulfur obtained in this procedure coagulated with difficulty and only after long heating. This precipitate filtered very slowly and had a tendency to become clogged up with colorless salt crystals as the solution cooled. The ash, however, dissolved fairly well.

In conclusion, it is our opinion that in neither method (1) nor in method (3) are interfering substances completely removed, and that this results in either incomplete sulfide precipitation or perhaps (later in the method) the formation of complex copper ions.

*J. L. Perlman.*—The acid hydrolysis method apparently does not recover the copper completely. The ashing method seems to be the easiest to apply and the results appear to be uniform and dependable. The acid digestion method yields higher values, which may in part be attributable to occluded matters, although this point should be definitely determined.



*J. H. Loughrey.*—While the crucibles containing the CuS from the ashing method were being ashed, the muffle was inadvertently turned up, and the copper was volatilized, as no copper could be found. Unfortunately the time was too short to permit another determination with the small amount of gelatin left.

Of the three methods for preparing the sample, the acid hydrolysis is the quickest, easiest, and apparently the most accurate. I prefer the  $H_2SO_4$  digestion to the ashing method; both are slow, but the latter is the slower of the two.

In view of the small number of collaborators reporting, no final conclusion would be justified at this time as to the definite superiority of any of the three methods for preparation of the sample. The results reported herein, however, point to the ashing method as the one likely to yield consistent and reasonably accurate results.

It is recommended<sup>1</sup> that collaborative work on the preparation of the sample be continued.

## REPORT ON SPICES AND OTHER CONDIMENTS

By HENRY A. LEPPER (U. S. Food and Drug Administration,  
Washington, D. C.), *Referee*

The studies this year were limited to those carried on by J. F. Clevenger on the determination of volatile oil in spices. Collaborative results reported led him to recommend the tentative adoption of methods. The collaborative results on total solids, acidity, nitrogen, and  $P_2O_5$  in salad dressings reported last year led to the recommendation for final adoption of these methods as official. There appears to be no urgent need for changes in the methods for starch and sugar in prepared mustard, and studies contemplated for the past several years may be postponed.

It is recommended<sup>1</sup>—

(1) That the methods submitted by the Associate Referee for the determination of volatile oils in spices, and for specific gravity, optical rotation, refractive index, eugenol, and acid and ester numbers of the separated oil, be adopted as tentative and further studied.

(2) That the methods for total solids, acidity, nitrogen and  $P_2O_5$  in salad dressings adopted last year as official (first action) be adopted as official (final action).

(3) That studies of methods for starch and sugars in prepared mustard be temporarily discontinued.

A paper entitled "Salad Dressing in General and French Dressing in Particular," by C. H. La Wall and W. E. Harrison, was presented.

<sup>1</sup> For report of Subcommittee C and action of the Association, see *This Journal*, 17, 60 (1934).

## REPORT ON VOLATILE OIL IN SPICES

By J. F. CLEVINGER (U. S. Food and Drug Administration,  
New York, N. Y.), *Associate Referee*

In accordance with the recommendations approved last year work was continued with the following collaborators:

O. C. Kenworthy and J. S. Ard, New York Station  
J. H. Cannon, Chicago Station  
L. H. McRoberts, San Francisco Station  
J. I. Palmore, Food Control Laboratory

Samples of whole sage in a paper bag and ground sage, pimento and nutmegs in sealed glass jars were sent to each collaborator, together with a copy of last year's report and additional suggestions. The results are shown in the table.

*Collaborative Results*

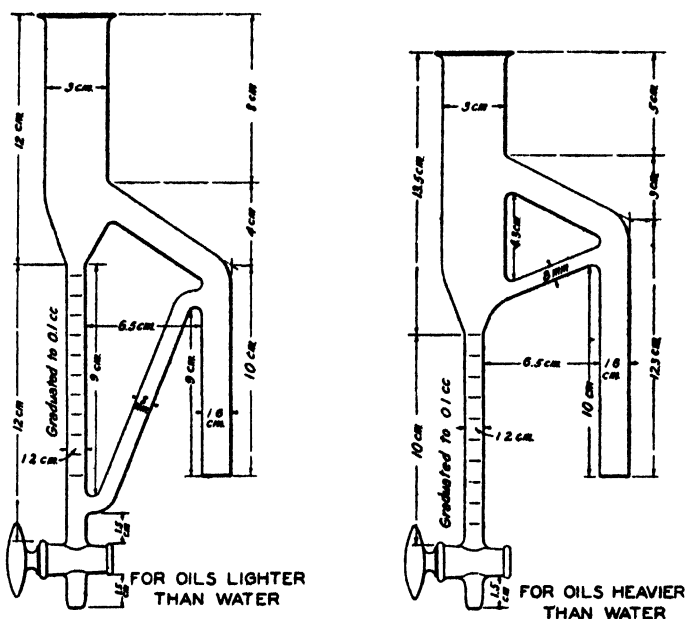
	CLEVINGER	ARD	CANNON	MCRBERTS	PALMORE	KENWORTHY
<i>Sage (unground)</i>						
Yield	1.81	1.8	1.85	1.6	1.8	1.77
Sp. Gr.	0.928	0.914	0.915	0.919	0.918	0.919
Op. Rot.	+3.46	+4.2	+3.6	+3.8	+5.9	+5.7
Ref. Ind.	1.467	1.464	1.463	1.463	1.462	1.465
Acid No.	1.2	0.8	1.6	1.4	2.5	2.1
Ester No.	19.1	8.4	27.3	10.0	12.4	9.7
<i>Sage (ground)</i>						
Yield	1.0	1.3	1.2	1.3	1.1	—
Sp. Gr.	0.938	0.928	0.921	0.929	0.928	—
Op. Rot.	+4.8	+6.0	+5.8	+5.8	—	—
Ref. Ind.	1.466	1.466	1.461	1.465	1.462	—
Acid No.	2.1	1.8	1.4	2.3	—	—
Ester No.	39.3	10.5	28.3	11.7	—	—
<i>Nutmeg (ground)</i>						
Yield	8.1	8.7	8.24	6.8	7.0	7.3
Sp. Gr.	0.916	0.906	0.904	0.909	0.907	0.921
Op. Rot.	+19.0	+21.1	+19.3	+19.4	+25.2	+16.0
Ref. Ind.	1.484	1.482	1.481	1.484	1.482	1.484
Acid No.	1.48	1.6	1.6	2.4	4.6	4.9
Ester No.	6.0	5.7	2.7	5.0	2.1	4.7
<i>Pimento (ground)</i>						
Yield	4.8	4.6	4.2	4.2	3.3	3.85
Sp. Gr.	1.043	1.039	1.036	1.038	1.042	1.038
Op. Rot.	-1.7	-1.1	-0.8	-1.4	-1.9	-0.9
Ref. Ind.	1.531	1.531	1.530	1.530	1.532	1.529
Eugenol	86	82	86	79	85	86

The results reported for the spices are more consistent than those reported for the same spices last year, indicating the practicability of the method. They also indicate a better understanding of the method by the collaborators.

Although the Associate Referee requested the collaborators to do their work soon after receiving the samples some determinations were not made until several months after. This is believed to account to some extent for the variation in the physical and chemical constants reported for the oils.

The methods have been published,<sup>1</sup> but the following cut should be substituted for the one shown on p. 72.

### TYPES OF OIL SEPARATORY TRAPS



### REPORT ON CACAO PRODUCTS

By J. W. SALE (U. S. Food and Drug Administration,  
Washington, D. C.), *Referee*

All three associate referees continued their work of improving the methods of analysis for cacao products. Each one submitted samples of known

<sup>1</sup> *This Journal*, 17, 70 (1934).

composition to collaborators and the results obtained justify recommendations for the adoption of new procedures to take the place of less satisfactory methods or to supplement the methods now in use.

*Milk proteins in milk chocolate.*—Offutt's modification of the present tentative method for the determination of casein gives results that are slightly high (about +0.15 per cent on the average), whereas the present tentative method gives somewhat low results (about -0.22 per cent on the average). The variation in results obtained by collaborators by the new procedure is less than in those by the old. These comments are based on both this year's and last year's results. In the new procedure the solution filters more rapidly, which is a distinct advantage. The data now available are quite extensive, and the adoption of the method as official in place of the present tentative procedure is therefore recommended.

*Cacao butter.*—The name of the new method for determining foreign fat in chocolate has been changed from "A" number to "Silver number." This latter designation gives some indication of the character of the method, whereas the name "A" number is non-descriptive. Work was discontinued on the "B" number. The three chief advantages of the new method, which is being recommended for adoption as a tentative method, were presented in the Referee's report for 1932.<sup>1</sup>

*Sucrose and lactose in milk chocolate.*—The additional collaborative work on the polariscopic method for sucrose and the copper-reduction method for lactose was conducted by six analysts under Fitelson's supervision and the results confirmed those obtained in the collaborative work of last year. The superiority of the new procedures is so evident that there is no hesitancy in recommending them for adoption as official.

It is now possible to apply the new methods for milk proteins and lactose and the tentative method for milk fat to the determination of milk solids and it is recommended that this be done next year.

It is believed that the work on cacao butter and lactose can be discontinued and that work on cacao shell will be desirable.

#### RECOMMENDATIONS<sup>2</sup>

It is recommended—

(1) That the tentative method for the determination of casein in milk chocolate, *Methods of Analysis, A.O.A.C.*, 1930, 157, be dropped.

(2) That the method described in last year's report [*This Journal*, 16, 563 (1933)] for the determination of milk proteins in milk chocolate be adopted as official (first action).

(3) That the method described in this year's report on cacao butter, for the determination of the silver number of fats, be adopted as tentative [*This Journal*, 17, 64 (1934)].

<sup>1</sup> *This Journal*, 16, 563 (1933).

<sup>2</sup> For report of Subcommittee C and action of the Association, see *This Journal*, 17, 61 (1934).

(4) That the polariscopic method for sucrose and the copper-reduction method for lactose described in the report for 1932 [*This Journal*, 16, 565 (1933)] be changed from tentative to official (first action).

(5) That further work on milk proteins, cacao butter, sucrose and lactose be discontinued except in connection with determination of milk solids.

(6) That work be renewed on the determination of cacao shell.

(7) That collaborative work be conducted on the determination of milk solids in milk chocolate.

## REPORT ON MILK PROTEINS IN MILK CHOCOLATE

By MARIE L. OFFUTT (U. S. Food and Drug Administration,  
New York, N. Y.), *Associate Referee*

The method proposed last year seemed to have some advantages over the present tentative A.O.A.C. method and gave more uniform results among the analysts. Two samples of milk chocolate were therefore sent out again this year with directions to determine the milk proteins by the tentative method, *Methods of analysis, A.O.A.C.*, 1930, p. 157 (Casein in Milk Chocolate), where casein  $\times 1.25$  gives milk proteins, and by the proposed method.<sup>1</sup>

### *Collaborative results* Per cent milk protein (Casein $\times 1.25$ )

COLLABORATOR	SAMPLE A (CALCULATED 2.67)				SAMPLE B (CALCULATED 3.46)			
	A O.A.C. METHOD		PROPOSED METHOD		A.O.A.C. METHOD		PROPOSED METHOD	
R. V. Bonner	2.13	2.16	2.47	2.55	3.01	3.15	3.67	3.72
J. Fitelson	2.44	2.35	2.77	2.92	3.09	3.38	3.99	3.88
W. T. Mathis	2.19	2.39	2.55		3.19	3.11	3.57	3.61
M. L. Offutt	2.30	2.24	2.70	2.88	2.89	3.03	3.75	3.73
J. Carol	2.60	2.68	3.29	3.11	3.58	3.58	4.50	4.40
W. O. Winkler	2.82	2.88	2.23	2.36	3.12			3.54
Max.		2.85		3.20		3.58		4.45
Min.		2.15		2.30		2.96		3.54
Av.		2.43		2.70		3.19		3.76
Var.		0.70		0.90		0.62		0.91

The collaborators were also requested to run duplicates and report the results as percentage of milk proteins, and to make nitrogen determination as directed in the official Gunning method, p. 20. 22.

The chemists reporting and to whom acknowledgment is made are the following, connected with the U. S. Food and Drug Administration: R.

<sup>1</sup> *This Journal*, 16, 563 (1933).

V. Bonner, San Francisco; J. Fitelson, New York; W. O. Winkler, Washington; J. Carol, Chicago; and W. T. Mathis, Conn. Agr. Exp. Sta., New Haven, Conn.

Mathis found that shaking the sample with 5 grams of magnesium carbonate after it had stood for four hours gave a clear filtrate.

Carol and Winkler found that solutions made in the proposed method are more easily filtered than those made in the A.O.A.C. tentative method.

The results obtained by the collaborators this year show more uniform agreement than they did last year. The results by the proposed method were generally higher than the calculated milk proteins while the A.O.A.C. tentative results were lower than the calculated. The results by the proposed method would have an advantage in calculating the total milk solids present. Other advantages of the proposed method were shown in last year's report.

It is recommended<sup>1</sup> that the proposed method for the determination of milk proteins in milk chocolates be adopted as official, first action.

## REPORT ON CACAO BUTTER

By W. O. WINKLER (U. S. Food and Drug Administration,  
Washington, D. C.), *Associate Referee*

That part of the method for the quantitative determination of foreign fat by means of the "A" number described in the report of 1931<sup>2</sup> was further studied. As a result of the experience gained in 1932 the method was modified with respect to details of saponification. The work was restricted to a study of the "A" number. The "B" number, which is a measure of the butter fat, was not studied as there are other suitable methods for this purpose, whereas the need for a method for the determination in cacao butter of foreign fat other than butter fat is very great. The "A" number is a determination of this latter type.

The designation "A" number is not descriptive. The term "Silver Number" is more fully descriptive of the method and will be used hereafter. A description of the revised procedure has been published.<sup>3</sup>

A sample of coconut butter (X) and a sample of a mixture consisting of 15 per cent of sample X and 85 per cent cocoa butter were submitted to each collaborator with a copy of the revised methods. The results obtained are given in Table 1.

The comments by collaborators were to the effect that the revision was an advanced step in the method for the detection of foreign fat. One col-

<sup>1</sup> For action of Subcommittee C and action of this Association, see *This Journal*, 17, 61 (1934).

<sup>2</sup> *This Journal*, 15, 549 (1932).

<sup>3</sup> *Ibid.*, 17, 84 (1934).

TABLE 1.—*Silver number of samples sent to collaborators*

COLLABORATOR	SAMPLE X (COCONUT STEARIN)		SAMPLE Y (15% COCONUT STEARIN, 85% COCOA BUTTER)		COCONUT STEARIN FOUND IN SAM- PLE Y BY MEANS OF THE SILVER NO.
					per cent
J. B. Wilson	26.5	Average 26.5	3.5	3.6	13.6
	26.5		3.7		
M. L. Offutt	28.6	28.6	4.3	4.4	15.4
	28.6		4.6		
R. L. Herd	25.7	25.7	3.1	3.1	12.1
W. T. Clarke	28.4	27.6	3.8	4.0	14.5
	26.0		4.8		
	28.2		3.5		
W. O. Winkler	26.1	26.4	3.1	3.1	11.7
	26.6		3.1		
—, —, Myers	26.6	26.4	3.0	3.1	11.7
	26.6		3.1		
	26.0		3.1		
Maximum		28.6		4.4	
Minimum		25.7		3.1	
Average		26.8		3.6	

TABLE 2.—*Silver number of commercial fats obtained by the associate referee*

LAB. NO.	TRADE DESCRIPTION	SILVER NUMBER
946	Coconut stearin pressed to M. P. 84°	39.6
947	Hard coconut butter (stearin with M. P. 90° and setting point 28.6°C.	34.3
951	Palm kernel stearin	27.4
952	Palm kernel stearin plus 23% coconut stearin	28.09
954	Coconut stearin 84°	34.4
939	Whole coconut oil 76°	53.5
955	Edible coconut oil 76°	55.7
956	Plastic hydrogenated coconut oil 92° from 76° oil made plastic by imbibing air	68.5
1	Cacao butter	0.7
2	Cacao butter	0.6
3	Dairy butter	11.6
4	Dairy butter	11.9

laborator reported that difficulty was sometimes encountered in securing sufficient filtrate from the magnesium precipitation, due probably to the

fact that a portion of the solution was retained on the filter in the form of an emulsion. This difficulty can be overcome by the addition of 20 cc. of water and by changing accordingly the factor used to calculate the silver absorbed per gram of fat.

The data in Table 1 show that when the silver number of the foreign fat is known, the proportion of foreign fat in mixtures of foreign fat and cacao butter can be closely approximated. The silver numbers of several commercial fats that may be used to adulterate chocolate are given in Table 2, together with silver numbers for cacao butter and dairy butter.

It will be noted at once from the data in Table 2 that the stearins have smaller silver numbers than has whole coconut oil. This is no doubt due to the fact that in the manufacture of the stearins, the fatty acids of lower molecular weight are largely removed. If the extracted fat hardens readily at room temperature, it is an indication that whole coconut oil is not present in appreciable amounts. While it is recognized that the method has limitations, it is believed that it will be found very useful in detecting adulteration with foreign fat.

#### RECOMMENDATIONS<sup>1</sup>

It is recommended—

- (1) That the method for the determination of the silver number described in this report be adopted as tentative.
- (2) That work on cacao butter be discontinued.

### REPORT ON SUCROSE AND LACTOSE IN MILK CHOCOLATE

BY J. FITELSON (U. S. Food and Drug Administration,  
New York, N. Y.), *Associate Referee*

Further collaborative studies of the methods for the determination of sucrose and lactose in milk chocolate, tentatively adopted last year, were carried out this year. The methods used are described in the report for 1932. Table 1 shows results obtained by the collaborators.

The results confirm the conclusions presented in the previous report. The polariscopic method for sucrose is trustworthy. The copper reduction method for lactose is superior to the optical method, and in the hands of an experienced analyst yields results within a few tenths of a per cent of the theoretical quantity present.

Attention has been called to an error in the copper reduction correction graph used in the lactose method.<sup>2</sup> The labels of the 250 mg. lactose  $\text{Cu}_2\text{O}$  and the 300 mg. lactose  $\text{Cu}_2\text{O}$  are obviously interchanged. A corrected graph is shown on p. 379.

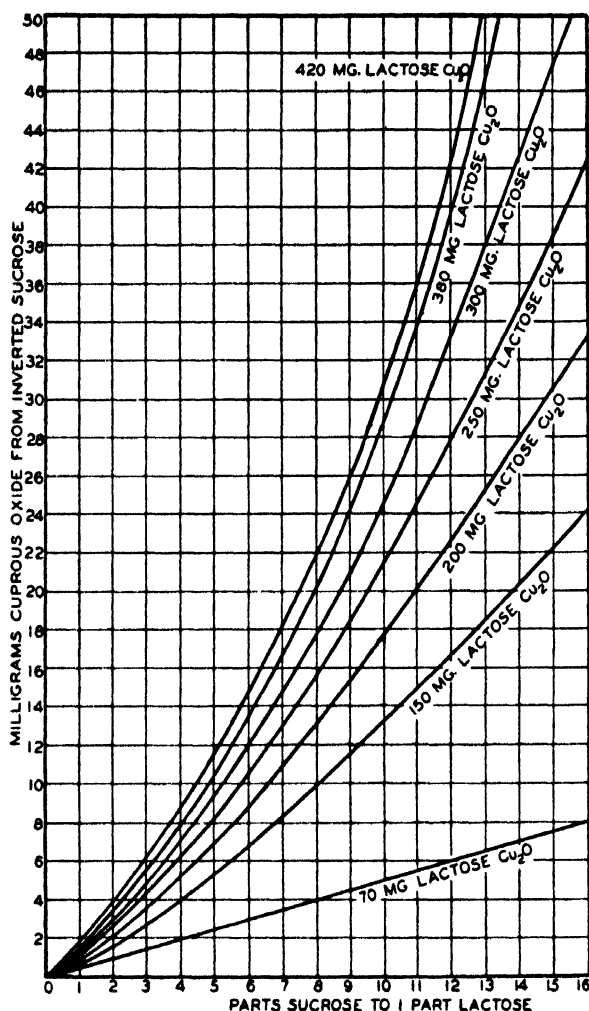
<sup>1</sup> For report of Subcommittee C and action of the Association, see *This Journal*, 17, 61 (1934).

<sup>2</sup> *This Journal*, 15, 556 (1932).



TABLE 1.—*Collaborative results (per cent)*

SAMPLE 7 (SUCROSE PRESENT—43.93%) (LACTOSE PRESENT—5.64%)				SAMPLE 8 (SUCROSE PRESENT—46.55%) (LACTOSE PRESENT—4.94%)		
COLLABORATOR	SUCROSE FOUND	LACTOSE FOUND BY—		SUCROSE FOUND	LACTOSE FOUND BY—	
		POLAR- SCOPE	COPPER REDUCTION		POLAR- SCOPE	COPPER RE- DUCTION
W. T. Mathis	44.48	6.09	5.78	46.82	5.83	4.97
	44.33	7.09	5.83	46.91	5.66	5.08
	44.33	6.86	5.84	46.78	5.88	5.14
Average	44.38	6.95	5.82	46.84	5.79	5.06
A. K. Klein	43.85	7.68	6.08	47.47	7.79	5.28
	43.80	8.40	6.02	47.33	7.15	5.23
Average	43.82	8.04	6.05	47.40	7.47	5.25
W. O. Winkler	44.36	5.89	5.03	46.35	5.44	4.32
	44.49	5.65	5.04	46.23	5.35	4.44
Average	44.43	5.77	5.04	46.29	5.40	4.38
J. Fitelson	43.59	6.20	5.74	45.90	5.72	5.22
	43.73	7.00	5.81	46.15	5.66	5.18
Average	43.66	6.60	5.78	46.03	5.69	5.20
M. L. Offutt	44.35	5.09	5.80	46.60	4.48	5.22
	44.35	5.09	5.83	46.97	4.65	5.19
Average	44.35	5.09	5.82	46.79	4.57	5.21
P. A. Mills	—	—	6.02	—	—	5.37
			6.01			5.35
Average			6.01			5.36
Maximum	44.49	8.40	6.08	47.47	7.79	5.37
Minimum	43.59	5.09	5.03	45.90	4.48	4.32
Average	44.13	6.49	5.75	46.67	5.78	5.07
Max. Var.	+0.56	+2.76	-0.61	+0.92	+2.85	-0.62

RECOMMENDATIONS<sup>1</sup>

It is recommended—

(1) That the polariscopic method for sucrose and the copper reduction method for lactose in milk chocolate described in the report for 1932<sup>2</sup> be adopted as official.

(2) That further study of sucrose and lactose in milk chocolate be discontinued and that this subject be closed.

<sup>1</sup> For report of Subcommittee C and action of the Association, see *This Journal*, 17, 65 (1934).

<sup>2</sup> *This Journal*, 16, 565 (1933).

## REPORT ON COFFEE

By E. M. BAILEY (Connecticut Agricultural Experiment Station, New Haven, Conn.), *Referee*

In the report last year<sup>1</sup> work done on methods for determining caffeine in coffee in which the caffeine content is of an order of magnitude of 0.2 per cent or less was cited and discussed. It was pointed out that micro methods are capable of giving values that may be regarded as exact; it also appears that ordinary macro methods with some precautions give results of a satisfactory degree of accuracy. It is apparent that without considerable experience in the technic of micro methods the high degree of accuracy of which such methods are capable may be completely lost.

The present official and tentative methods for the determination of caffeine in coffee make it obligatory to estimate caffeine on the basis of nitrogen in the caffeine residue. If the residues from duplicate determinations of caffeine are combined for the determination of nitrogen, the usual quantities of reagents used in digestion are reduced one-half, and the tubes of the distillation apparatus are thoroughly steamed before distillation is made, satisfactory results will be obtained. The analyst should in all cases check his results by means of suitable controls with the reagents and apparatus used.

It is recommended<sup>2</sup> that the language of the present official and tentative methods be not changed, but that an explanatory note be added to suggest the precautions that should be taken when dealing with products very low in caffeine, that this note be inserted in *Methods of Analysis*, A.O.A.C., 1930, Chap. XVIII, under Sec. 14, p. 151, and that a reference to this note be made under Sec. 15, p. 152, thus:

In the case of products very low in caffeine combine the caffeine residues from duplicate determinations (thus representing 20 g. of original material) and determine nitrogen as directed in II, Sec. 19 or 22, using half the quantity of reagents called for in the digestion and steaming out the distillation apparatus thoroughly before distilling. Distil to small volume in the distilling flask to insure removal of all ammonia. Correct for the blank obtained, using the same reagents and apparatus and pure sucrose in place of caffeine.

## REPORT ON GUMS IN FOODS

By L. J. CROSS (State Department of Agriculture,  
Ithaca, N. Y.), *Referee*

No collaborative work was done the past year for the reason that there are no general methods for the detection of gums in foods worthy of consideration by this Association. The Referee gave his undivided attention

<sup>1</sup> *This Journal*, 16, 567 (1933).

<sup>2</sup> For report of Subcommittee C and action of the Association, see *This Journal*, 17, 61, 63 (1934).

to the development of methods. In this broad and difficult field research was confined to cream cheese, ice cream, mayonnaise, salad dressing, and kitchen dressing, and to the detection of locust bean gum and gum tragacanth.

This work upon methods has progressed so well that it will be possible to invite collaboration of those interested in this field next year.

## REPORT ON FATS AND OILS

By GEORGE S. JAMIESON (Bureau of Chemistry and Soils,  
Washington, D.C.), *Referee*

During the past year collaborative study was completed on methods for the analysis of cottonseed. These are the methods given in U. S. Department of Agriculture Agricultural Economics, S.R.A., No. 133, entitled "The Official Standards of the United States for the Grading, Sampling and Analyzing of Cottonseed Sold or Offered for Sale for Crushing Purposes."

The particular methods to which reference has been made are the following: (1) Laboratory sample; (2) determinations of percentage of foreign matter; (3) mixing and quartering; (4) moisture; (5) preparation of seed for oil and ammonia determinations; (6) moisture determination of ground sample; (7) oil; (8) ammonia; and (9) free fatty acids.

The results obtained in the analysis of four samples of cottonseed by nine collaborators are given in the table on the next page.

In view of the favorable results shown in the table, as well as those obtained on 24 other samples for which space is not available in this report, it is recommended that these methods be made official.

## RECOMMENDATIONS<sup>1</sup>

It is recommended—

(1) That the methods for the analysis of cottonseed mentioned in this report be made official (first reading).

(2) That the study of the refractometric method for the determination of oil in oleaginous seeds be continued.

(3) That an associate referee be appointed on fat and oil analysis.

(4) That collaborative study be undertaken on the determination of the hydroxyl number of fats and oils in comparison with the acetyl value determination.

(5) That collaborative study be undertaken on the preparation of aldehyde-free alcohol to determine the procedure best adapted for preparing this reagent.

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<sup>1</sup> For report of Subcommittee C and action of the Association, see *This Journal*, 17, 61 (1934).

LABORATORY	FOREIGN	OIL	AMMONIA	FREE FATTY ACIDS	MOISTURE
	<i>per cent</i>	<i>per cent</i>	<i>per cent</i>	<i>per cent</i>	<i>per cent</i>
Barrow-Agee	0.1	20.3	3.28	0.4	10.8
"	0.0	19.9	3.16	0.6	10.5
"	0.4	20.9	3.23	0.5	10.3
"	0.0	20.0	3.18	0.5	10.8
"	0.3	20.6	3.25	0.7	10.6
T. C. Law	0.1	20.4	3.30	0.6	10.9
"	0.2	20.5	3.22	0.4	10.5
"	0.3	20.1	3.25	0.5	10.1
R. S. McKinney	0.2	20.3	3.24	0.5	11.0
Barrow-Agee	0.1	18.2	3.72	3.0	13.0
"	0.0	18.2	3.71	3.0	13.0
"	0.2	18.4	3.74	3.1	12.9
"	0.2	18.2	3.64	2.6	13.0
"	0.0	18.6	3.82	2.3	12.0
T. C. Law	0.1	18.7	3.69	2.8	13.0
"	0.1	17.9	3.63	3.6	13.1
"	0.3	18.5	3.72	3.5	11.9
R. S. McKinney	0.0	18.5	3.68	3.4	13.1
Barrow-Agee	0.5	19.1	3.89	2.4	6.8
"	0.6	19.2	3.93	2.6	7.1
"	0.4	19.2	3.93	2.8	7.1
"	0.4	19.3	3.92	2.6	6.8
"	0.4	18.7	4.03	2.5	7.1
T. C. Law	0.4	19.5	3.92	2.8	6.9
"	0.6	19.3	3.82	2.2	7.0
"	0.3	19.8	3.97	3.6	6.3
R. S. McKinney	0.3	19.6	4.00	2.4	6.6
Barrow-Agee	0.1	17.9	3.82	6.5	12.1
"	0.0	18.8	3.83	7.0	12.0
"	0.0	17.8	3.77	6.5	12.0
"	0.1	17.9	3.78	6.0	12.2
"	0.0	17.6	3.88	6.0	12.2
T. C. Law	0.0	17.8	3.86	6.0	11.9
"	0.1	17.5	3.81	6.5	12.1
"	0.1	17.9	3.87	6.0	12.1
R. S. McKinney	0.0	17.6	3.86	5.5	12.3

No report on the determination of oil in oleaginous seeds was given by the associate referee.

## REPORT ON MICROCHEMICAL METHODS

By E. P. CLARK (Bureau of Chemistry and Soils,  
Washington, D. C.), *Referee*

So far as the Referee is aware, the system of semi-micro analytical methods presented to this Association last year has not met with favor.

This is perhaps due to the fact that the procedures thus far advocated are essentially for ultimate rather than proximate analysis, and also to the fact that few laboratories are equipped with the necessary apparatus for the work. Consequently, during the past year no collaborative work was conducted.

Interest in the project, however, has continued, and detailed procedures for the determination of carbon and hydrogen and Dumas nitrogen have been published.<sup>1</sup>

Because of the possibility of using iodo compounds as insecticides simple and convenient semi-micro methods for the estimation of both aliphatic and aromatic iodine have been developed.

The semi-micro volumetric method for methoxyl and ethoxyl groups has been used extensively in a number of laboratories with uniform success. For this reason it is recommended<sup>2</sup> that the method, as published,<sup>3</sup> be adopted as a tentative procedure.

## REPORT ON MICROBIOLOGICAL METHODS

By ALBERT C. HUNTER (U. S. Food and Drug Administration,  
Washington, D. C.), *Referee*

The development of approved or standard methods for the microbiological examination of foods presents a wide field of possible activity with a bewildering number of factors that must be considered. This is particularly evident at the beginning of the undertaking, as in the present case, this being the first report of the Referee on Microbiological Methods. A question that immediately presents itself is whether work should be undertaken on a broad scale, involving many different food products, or whether, at the beginning, investigations should be restricted to some particular class of foods until those collaborating in this field become oriented. After considering various factors the Referee concluded that the latter alternative should be adopted.

In organizing a program for the development of such methods the first step is to select a type of food product. For the time being, microbiological methods for the examination of water, milk, and oysters may be ignored as there already exist standard methods for the examination of these products sponsored by the American Public Health Association, and by other organizations as, in the case of milk, the American Dairy Science Association and the International Association of Dairy and Milk Inspectors, and, in the case of water, the American Water Works Association. At the present time committees from the American Public Health Association

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<sup>1</sup> *This Journal*, 16, 414, 575 (1933).

<sup>2</sup> For report of Subcommittee C and action of the Association, see *This Journal*, 17, 62 (1934).

<sup>3</sup> *This Journal*, 15, 136 (1932).

and the American Dairy Science Association are actively functioning in a program to develop approved methods for the bacteriological examination of foods in general, and especially of dairy products such as dry milk, ice cream and butter.

In order to avoid unnecessary duplication and conflict, the work of this Association on microbiological methods should be planned and prosecuted in cooperation with these other associations. Conferences already held with members of the American Public Health Association committee have established a basis for the necessary cooperation. In the selection of associate referees and collaborators for the work of this Association, and in the appointment of committees from other interested organizations, it is extremely desirable that there be some intermingling of personnel of the various groups to assure that methods developed and approved by one association may be jointly approved by the others.

Confronted then with a knowledge of existing standard methods for the microbiological examination of some foods, and cognizant of the activities of committees from other organizations, the Referee gave careful thought to where the work of this Association may be begun to avoid unnecessary duplication. As an aid to this study during the past year he conducted an inquiry designed to provide data that would form the basis of this report and make possible certain definite recommendations.

A form letter was sent to thirty-three bacteriologists who are actively engaged in food work; sixteen are engaged in regulatory work in state or municipal laboratories, sixteen are conducting research work on foods in university or trade association laboratories, and one is operating a commercial consulting food laboratory. The letter contained the following paragraph: "At the outset of the work I should like to recommend to the Association for study some food product with which practically all food bacteriologists have to deal, and for the examination of which the bacteriological technic is relatively simple, and yet entails in different laboratories sufficient diversity of method to warrant study for the purpose of eventually formulating directions for a standard procedure. With this in mind I have thought that the general class of canned food products offers a fertile field. A routine sterility test of canned foods is a relatively simple operation, and yet fraught with more pitfalls for the bacteriologist than are some more technically difficult operations. I should be glad to receive from you comments as to whether or not you believe this subject of sufficient importance to warrant such study as may properly be given it by collaborators of the A.O.A.C. If the need for methods for some other class of products appeals to you as of more importance I should like to receive suggestions."

Replies were received from twenty-nine of the thirty-three persons to whom the letter was addressed, three regulatory officials, and one research

worker failing to answer. Of the twenty-nine bacteriologists who replied, twenty-four expressed themselves in favor of attacking the problem of developing standard microbiological methods for canned foods; three did not commit themselves as "for" or "against," but confined their remarks to other questions submitted to them, and two voted "no" without suggesting any alternative. One correspondent stated that he was in favor of what might be termed "approved" methods but was opposed to inflexible "standard" methods. A suggestion was made that the A.O.A.C. formally accept the American Public Health Association methods for milk, water, and oysters, and the American Dairy Science Association methods for ice cream and butter. On the other hand, suggestions were made that the A.O.A.C. undertake some critical study of the present standard methods for oysters, milk, and water. Six correspondents who favor a study of canned foods also recommended that some attention be given to fresh vegetables, dried foods, frozen foods, crustacea meats, chicken, ground or chopped meats, and materials from food poisoning outbreaks. These suggestions are excellent and represent in part the scope of the field. If canned foods are approved as the object of study now, these other products are to be listed for future attention.

In the general class of canned products is included a wide variety of types of foods such as vegetables, fruits, meat, fish and dairy products. The area of production is widespread and consumption of canned foods is almost universal. Problems dealing with canned products frequently confront the regulatory official. The technic for a bacteriological examination of such products, adapted to the particular problem at hand, is not adequately described for the guidance of the analyst and the administrative official is frequently confused when attempting to compare the results of examinations made in different laboratories. It is a certainty that the publication of approved methods for the bacteriological examination of canned foods would receive a general welcome.

With the letter mentioned previously there were transmitted eleven questions designed to disclose to just what extent diversity of method exists in the bacteriological examination of canned foods. The questions were somewhat restrictive in character, but in formulating them the purpose in mind was to provoke a discussion of the basic and fundamental procedures for testing sterility of canned foods, leaving for some future period discussions of modified procedures for specific problems. It has been pointed out repeatedly, however, by a number of correspondents that methods for the bacteriological examination of canned foods must be developed with specific problems in mind. It certainly follows that studies of bacteriological methods for canned foods must take into consideration the variety of specific spoilage problems common to this type of food product. Nevertheless, the answers to the questions submitted may be reviewed from the viewpoint originally intended. Replies to these



questions are interesting, and many thanks are due those correspondents who so willingly answered.

In reply to the question "What treatment is given the exterior of the cans to cleanse or sterilize them before opening?" it was learned that there are at least nine different methods of treatment used by the twenty-seven laboratories from which answers were obtained. In some laboratories it is deemed sufficient to burn alcohol on the lid to be opened; in other laboratories the cans are scrubbed with soap and water before flaming. Other bacteriologists reported the use of phenol or hypochlorite. Because of the possibility of contamination from the outside of the can, this operation is important and is worthy of careful study.

Questions 2 and 3 related to the type of room or chamber in which sterility tests are made, and also to the kind of instrument used in opening or venting the can. In regard to the type of room, it developed that the correspondents are about equally divided in their use of an open laboratory and a small, special inoculating room. Also the answers were about equally divided between the use of an ordinary sterilized can opener and some form of sterile punch, such as an awl, a nail, an ice pick, or a screw-driver.

The fourth and fifth questions asked what type of pipet was used for subsampling liquids in cans and what means of suction were employed for withdrawing the liquid. It was learned that the variety of pipets used ranges from the ordinary 1 cc. bacteriological pipet to a large untapered length of glass tubing. In the majority of cases suction is applied by mouth, but when dangerous products are suspected, the use of a bulb on the pipet is quite general. An inquiry (Question No. 6) as to the instrument used for obtaining subsamples, or inoculum from solid materials in cans, elicited the information that use is made of forceps, a spoon, a spatula, a scalpel, or any other instrument that can be easily sterilized and handled with aseptic precautions.

Questions 7 and 8 were as follows: "In sampling products containing both solid matter and liquid, do you use as inoculum the solids, liquid or both?", and "What amount of inoculum is usually taken from each can?" In reply to Question 7, seventeen correspondents stated that they use both solids and liquid, six stated that they use liquid only, and two stated that the answer depends upon the product. Two others did not specifically answer this question. This step in the bacteriological examination of canned foods may have considerable influence on the results obtained and is a fruitful topic for investigation. The point covered in the eighth question is extremely important. One correspondent replied: "I agree that there is no greater error in all of our work than in sampling. I would, therefore, like to see your committee give this phase of the work considerable study." In Table 1 are given the replies received regarding the amount of material used as inoculum; it varies from as little as one

drop to as much as 50 grams. From twenty-seven laboratories replying to this question twenty different answers were obtained. It is recognized that the consistency and character of the product dictate how much should be taken but because of the fundamental importance of an adequate sample this step in the procedure needs particular attention.

Two questions, 9 and 10, were prepared to ascertain what culture media are used for testing non-acid and acid products. Both these questions brought a variety of answers. It was learned from twenty-six laboratories replying to these questions, that in culturing non-acid products six laboratories depend on only one medium, nine laboratories utilize two media, three use three different media, six use four media, and two depend on several special media prepared for the case under examination (Table 2). The information collected shows that seventeen well-known, ordinary types of culture media and a number of specially prepared media are used for growing microorganisms from non-acid products. The answers to this question regarding acid foods show an even greater variety of media used. Of the twenty-six laboratories replying, nine depend on one medium, seven use two media, two use three media, one use five, and seven use several specially prepared culture media. For the examination of acid foods, twenty-one well-known laboratory media were reported, and, in addition a variety of special culture media prepared for the particular product under examination.

TABLE 1.—*Amounts of inoculum used by different laboratories in the bacteriological examination of canned foods*

INOCULUM	LABORATORIES
1 drop to 2 or 3 cc.	1
0.1 cc. to 10 cc.	1
1 cc.	5
1 to 2 cc.	1
1 to 2 cc. per tube (16 tubes)	3
2 cc.	1
1 to 5 grams	1
3 grams	1
4 cc.	1
1 to 10 grams	1
5 to 10 grams	1
10 grams	1
Not less than 10 grams (frequently more)	1
10 to 15 grams	1
10 to 20 grams	1
10 to 100 grams	1
Solids 20 grams; Liquid 1 cc.	1
25 to 30 cc.	1
Solids 50 grams; Liquid 10 cc.	1
Indefinite—variable	2

The last question in the series (No. 11) inquired concerning the time and temperature of incubation of cultures. Practices as to incubation vary remarkably. From twenty-six laboratories replying to this question, thirty-one different combinations of time and temperature were reported, the variation, of course, being mostly in the time of incubation since the temperatures at which incubation is carried out are more constant than the period of time allowed for bacterial growth. The periods of incubation vary from 48 hours to 30 days. The following summary shows the temperatures of incubation used by the twenty-six laboratories from which figures were obtained.

TEMPERATURES	LABORATORIES
37°C. only	9
37°C. and 55°C.	8
37°, 55°, and 20°C.	4
37°, 55°, 20°, and 30°C.	2
37° and 20°C.	1
37°, 44°, and 20°C.	1
37°, 33°, and 55°C.	1

The answers to Questions 9, 10, and 11 particularly indicate the need for some standardization or, at least, some simplification of the methods now used for the bacteriological examination of canned foods. All the information collected leads to the inescapable conclusion that the method of examining canned foods bacteriologically depends to a great extent on the ingenuity of the analyst and on the availability of certain apparatus and culture media.

Certain points covered by the questions discussed here are relatively unimportant, and although an approved method would contain instructions for some of these steps deviation from the recommendation would not necessarily adversely affect the results. For example, if the work is done carefully the type of room, within reasonable limits, in which the examination is made is not important. Also the kind of instrument used for opening the can, the pipet, the method of withdrawing liquids, and the instrument used for solid products do not matter particularly if precautions are taken to sterilize the implements and to follow aseptic procedures. On the other hand, the type of material and the quantity of inoculum are important and are basic factors from which to draw correct conclusions, as is also the selection of suitable culture media and of incubation times and temperatures for the purpose of the examination. If canned products are selected as a class of foods upon which to begin study for the development of methods, the points just mentioned should receive early attention.

After consideration of the subject in the light of the information elicited from food bacteriologists during the year, the Referee considers that necessary steps should be taken to organize work for the development of

TABLE 2.—*Different culture media used by various laboratories for bacteriological examination of non-acid and acid canned foods*

LABORATORY	NON-ACID PRODUCTS	ACID PRODUCTS
A	3	5
B	1	1
C	2	2
D	3	3
E	2	Several special media
F	1	Several special media
G	2	1
H	1	2
I	4	3
J	3	Several special media
K	2	2
L	1	1
M	4	1
N	2	1
O	2	1
P	1	1
Q	Several special media	Several special media
R	1	1
S	4	2
T	4	1
U	2	2
V	No reply	No reply
W	Several special media	Several special media
X	4	Several special media
Y	2	2
Z	2	2
*	4	Several special media

methods for the microbiological examination of canned foods in general; in other words, for a study of basic and fundamental technic for testing sterility of foods in hermetically sealed containers.

#### RECOMMENDATIONS<sup>1</sup>

It is recommended—

(1) That studies of methods for the microbiological examination of canned foods be undertaken.

(2) That five associate referees in this field be appointed.

(3) That the investigations be planned to give special attention to (a) treatment of the container before opening, (b) proper subsampling procedures, (c) suitable culture media for non-acid products, (d) suitable culture media for acid products, and (e) times and temperatures of incubation.

<sup>1</sup> For report of Subcommittee C and action of the Association, see *This Journal*, 17, 62 (1934).

## CEREAL SECTION

## REPORT ON CEREAL FOODS

By J. A. LeCLERC (Bureau of Chemistry and Soils,  
Washington, D. C.), *Referee*

Those who have been meeting with the A.O.A.C. for a number of years will appreciate the superior condition existing today. In the main auditorium, with a few chemists scattered here and there, it was difficult to hear and it was almost impossible to initiate any discussion. This small room is being used for the third time, and the scheme of having a few extra papers besides the referee's reports has been continued. The referee's reports are good, and it is to them that the success of the meeting is due, but an occasional paper sandwiched in between the reports makes a good program.

It is interesting to read a report of the First International Congress of Panification, which was held in Rome, June, 1932. That report contains many valuable papers of interest to cereal chemists. It is also interesting to note therein a suggestion made to standardize the international methods applicable to the study of bread, flour, and baked products. Three years ago this move was anticipated by this Association, and an associate referee was appointed to study foreign methods for testing flours. It is regretted by the Referee that he is not able to report on that subject.

At that convention in Rome there were representatives from 17 European countries and from 5 countries of South America, as well as representatives from Canada. This country, which in normal times boasts of a billion dollar milling industry and a billion dollar baking industry, with cereal chemists in various government departments and in the numerous Experiment Stations, had no representative. This is rather deplorable, and it is hoped that at the next meeting of that kind an American representative may be present.

Considerable progress has been made in the last few years, but all progress is not confined to this hemisphere. That is evident from the common usage of the Brabender machine and the Chopin extensimeter in European countries for the purpose of evaluating the quality of flour. This Association should plan to enlarge its scope of activities. Now that the 18th Amendment is about to be discarded these activities should include barley and malt and products of corn and rice, which are used in the brewing and distilling industries, as well as wheat and rye.

The recommendations of the General Referee were approved by Committee C and by the Association. They are incorporated in the report of Committee C, *This Journal*, 17, 57 (1934).

A paper, entitled "Products of Corn" was presented by H. E. Barnard, Indianapolis, Ind. An abstract of this paper was published in *Cereal Chemistry*, 11, 100 (1934).

REPORT ON ASH IN FLOUR, ALIMENTARY PASTE, AND  
BAKED PRODUCTS; CHLORIDES IN FLOUR AND  
BAKED PRODUCTS; AND  
COLOR IN FLOUR

By D. A. COLEMAN (Grain Division, U. S. Bureau of Agricultural  
Economics, Washington, D. C.), *Associate Referee*

The work for this season has been entirely exploratory, with entire concentration of thought on the subject of color in flour. No collaborative work was undertaken in this field for the reasons developed later.

The Associate Referee was confronted with the fact that there are at least four different devices used to measure color in flour. These may be subdivided into methods that measure the color of the flour directly, and those that express the color of flour in terms of the extract.

Under the first classification are (1) the older Munsell color device, which is described by Dorothy Nickerson in U. S. Department of Agriculture Bulletin No. 154, Color of Agricultural Products; (2) the newer Wallace-Tiernan device with which the color is examined, after it has been wetted, by means of Maxwell discs; (3) a device now being developed by the Bausch and Lomb Company; and (4) devices by which measurement of the color of the flour is attempted by the use of photoelectric cells. Some of these devices have been cited in foreign literature, and one of recent manufacture in this country has been placed on the market by the Western Electric Company.

In the second class the devices in more common use are (1) the spectrophotometer used by Ferrari and Bailey; (2) the old gasoline colorimeter method modeled after Winton's earlier work; (3) the method of Kent-Jones and Herd; and (4) a modification of the method mentioned in Item 4, Class 1, in which an extraction is made and the color of the flour determined by means of a photoelectric cell. This new departure is being sponsored by the Laboratory Construction Company, Kansas City, Missouri.

With such a multitude of devices and methods available in the trade, but with none available in the laboratory of the Associate Referee until late this year, it was impossible to make any worth-while studies of the effectiveness of these instruments, and particularly to decide on any one device that would serve as a common instrument in the hands of many.

In spite of the fact that it accurately determines the extent of pigmentation in a sample, the high initial expense of the spectrophotometer will

probably militate against its extensive use. It has likewise been demonstrated quite conclusively that the ordinary colorimeter does not determine color in extracts accurately, therefore it can be eliminated from the field. Just what the photoelectric cell may do in relation to the estimation of color seems to depend upon the securing of the proper cell, and it may be necessary to have several cells to determine different ranges in pigmentation.

This disposal of possible methods practically preempts the extraction field and leaves those instruments that measure color of products directly, such as the color-measuring devices described by Nickerson, Wallace and Tiernan, and the Bausch and Lomb Company. With the first two devices the color is matched microscopically by means of a telescope, and the sample, as well as the color discs, is in rotation. This is somewhat of a disadvantage because it is necessary to stop the rotation of the discs and/or sample in order to permit the observer to change the proportion of colors on the color discs in matching the fields in the telescope. Also, with the Wallace-Tiernan device more desirable results obtain if the sample is wetted, and furthermore, with this device it is now only possible to evaluate color in terms of red, black, white and yellow. No formula appears to be available to reduce these color variances to a single term as is the case with the Munsell system. However, through the splendid cooperation of Miss Nickerson, this desirable factor may be brought about with little effort.

The first demonstration of the new Bausch and Lomb machine shows that it is one of the most desirable instruments available for direct color measurement. Both the discs and the sample remain stationary, and the color prisms are located in the shaft of the motor, thus making possible rapid and easy measurements.

It is the Associate Referee's opinion that the subject of measurement of color in flour can wait on the development of this new instrument. The general conclusions presented with respect to the Wallace-Tiernan instrument are quite in line with those presented by Baker, Parker, and Frees.<sup>1</sup>

The pressure of other work and the decided curtailment of personnel made it impossible to carry on the other duties assigned.

## REPORT ON H-ION CONCENTRATION OF FLOUR

By R. J. CLARK (436 W. Dartmouth Road, Kansas City, Mo.),  
*Associate Referee*

One of the questions that arose during the collaborative work conducted on the colorimetric determination of the H-ion concentration of

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<sup>1</sup> *Cereal Chem.*, 10, 437 (1933).

flour a year ago related to the indicator best suited for this determination. Until recently the writer used bromcresol purple, range  $pH$  5.2–6.8, but so much trouble was experienced with this indicator from dichromatism (production of color shades that do not occur in the list of color standards) that in recent years paranitrophenol, range  $pH$  5.4–7.0, has been used with much better success.

When a flour of  $pH$  lower than 5.4 was found  $\gamma$  (2:5) dinitrophenol, range  $pH$  4.0–5.6, was used. Both these indicators have a color change from colorless to deep yellow. In order to facilitate readings with them, a piece of blue glass was placed over the slots on the side of the block comparator opposite the etched glass. No difficulty was experienced from dichromatism when these indicators were used. It is therefore suggested that  $\gamma$  (2:5) dinitrophenol, range  $pH$  4.0–5.6, and paranitrophenol, range  $pH$  5.4–7.0, be considered for collaborative work on the colorimetric determination of flour  $pH$ .

The Associate Referee has used the following method for the colorimetric determination of bread  $pH$  successfully:

Weigh 10 grams (or some multiple thereof) of bread prepared as directed in *Methods of Analysis*, A.O.A.C., 1930, 177, 46, into a clean, dry Erlenmeyer flask and add for each 10 grams of bread 100 cc. of distilled water at a temperature of 25°C. Shake or whirl the flask until the particles of bread are evenly suspended and the mixture is free from lumps. Place in a thermostat at 25°C. and shake intermittently in such a manner as to keep the bread particles in suspension for 30 minutes. Let stand quietly for 10 minutes, then decant the supernatant liquid into the colorimetric H-ion vessels and immediately determine its H-ion concentration by comparison with suitable colorimetric standards, preferably paranitrophenol, range  $pH$  5.4–7.0, or  $\gamma$ (2:5) dinitrophenol, range  $pH$  4.0–5.6.

It will be noted that the procedure for the colorimetric determination of  $pH$  in bread is practically the same as that for flour, which was studied last year.

#### RECOMMENDATIONS

It is recommended<sup>1</sup>—

(1) That  $\gamma$  (2:5) dinitrophenol, range  $pH$  4.0–5.6, and paranitrophenol, range  $pH$  5.4–7.0, be used in making colorimetric  $pH$  determinations on flour; and that since the color change of both these indicators is from colorless to deep yellow, a blue glass be placed over the slots on the comparator block opposite the etched glass to facilitate the readings.

(2) That the method for the colorimetric determination of  $pH$  in bread as outlined be used and that both methods be studied collaboratively.

<sup>1</sup> For report of Subcommittee C and action of the Association, see *This Journal*, 17, 58 (1934).



## REPORT ON DIASTATIC VALUE OF FLOUR

By M. J. BLISH (Agricultural Experiment Station of Nebraska,  
Lincoln, Neb.), *Associate Referee*

This report is substantially an endorsement of the method proposed in the "supplementary" portion of last year's (1932) report,<sup>1</sup> which dealt with a procedure for the estimation of maltose based upon the ferricyanide method of Hagedorn and Jensen.<sup>2</sup> As compared with some of the better known types of copper reduction methods, and with the picric acid colorimetric method, the ferricyanide method is superior from the standpoint of accuracy, reliability, simplicity, and convenience, in the opinion of the Associate Referee and of many cereal chemists who are now using the method in industrial control work.

Gore<sup>3</sup> has recently proposed a polarimetric method for the estimation of the saccharogenetic power of flour. The applicability of the polarimeter for this purpose cannot be denied. From the standpoint of establishing a suitable and convenient standard or "official" method, however, the polarimetric procedure, in the opinion of the Associate Referee, has certain objectionable features that are not to be found in the proposed ferricyanide method. A few of these are the following:

1. A first-class polarimeter is an expensive item of equipment not available to the majority of cereal technologists, especially in the industrial laboratories.

2. The polarimetric method requires a sample five times larger and correspondingly larger quantities of clarifying reagent (sodium tungstate) than does the ferricyanide method.

3. Flour extracts are occasionally encountered which are not sufficiently clear to permit satisfactory readings in the polariscope, the occurrence of this troublesome condition being relatively more frequent with the lower grade flours, or with flours containing sprouted malted wheat preparations.

4. The use of the polarimetric procedure requires a relatively high incubation temperature (37°) in order to keep the incubation period within reasonably convenient time limits. The ferricyanide method, on the other hand, permits a comparable incubation period at a temperature of 30°, which is comparatively much closer to the fermentation temperature actually used in bread baking.

5. In the polarimetric procedure, a blank or check determination on a non-incubated flour extract must always be made. This step is necessitated by the fact that, as found by Blish, Sandstedt and Astleford,<sup>4</sup> flours contain substantial and variable quantities of sucrose. Sucrose is obviously a factor influencing polarimetric readings, but, being non-reducing, it is without influence in the ferricyanide method. The quantity of *reducing sugars* originally present as such in sound, normal flour, on the other hand, is so small and so nearly constant that in dealing with such flours the blank or check determination for all practical purposes may be entirely eliminated. This involves a very considerable saving of time, work, equipment, and reagents.

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<sup>1</sup> *This Journal*, 16, 497 (1933).

<sup>2</sup> *Biochem. Z.* 135, 46-58 (1923).

<sup>3</sup> *This Journal*, 16, 403 (1933).

<sup>4</sup> *Cereal Chem.*, 9, 378 (1932).

These features appear to justify a preference for the ferricyanide modification of the Rumsey type of procedure.

The details and specifications of the proposed ferricyanide method are essentially as they appear in last year's supplementary report,<sup>1</sup> and as published elsewhere by Blish and Sandstedt.<sup>2</sup>

The purpose of the present report is to present a final and slightly revised statement of the method, also to cite results of collaborative tests conducted during the past season with the ferricyanide method as adapted to the estimation of the maltose produced by diastasis in flour suspensions.

#### COLLABORATIVE TESTS

Collaborative tests on two flours, A and B, were participated in by 18 different laboratories, using specifications as recently published by Blish and Sandstedt.<sup>2</sup> Each collaborator was asked merely to estimate the total content of reducing sugars (as maltose) in the flour extracts after 1 hour's diastasis, and to report values in terms of mg. of maltose per 10 grams of flour. Each collaborator made duplicate or triplicate (or more) determinations on each sample. As the replicated determinations of each individual collaborator agreed very closely, only average results for each collaborator are shown in Table 1.

TABLE 1.—*Results of collaborative diastatic activity tests*

COLLABORATOR	SAMPLE A	SAMPLE B
<i>mg. of maltose per 10 grams of flour in 1 hour</i>		
1	318	160
2	316	155
3	302	157
4	304	170
5	300	160
6	327	167
7	301	159
8	307	155
9	316	163
10	319	160
11	324	156
12	322	160
13	—	156
14	304	167
15	285	175
16	260	150
17	286	156
18	265	147
Av.	303	160

<sup>1</sup> *Loc. cit.*

<sup>2</sup> *Cereal Chem.*, 10, 189-202 (1933).

During the months of June, July, and August, respectively, collaborative tests of the ferricyanide method were conducted among some of the members of the Pioneer Section of the American Association of Cereal Chemists. Upon each of these occasions a sample of flour was sent to those members desiring to collaborate. With the kind permission of H. W. Putnam, Chairman of the Pioneer Section, the results of these tests are presented in Table 2.

TABLE 2.—*Results of collaborative diastatic activity tests conducted by the Pioneer Section of the A. A. C. C.*

COLLABORATOR	JUNE SAMPLE	JULY SAMPLE	AUGUST SAMPLE
<i>mg. of maltose per 10 grams of flour in 1 hour</i>			
1	355	178	266
2	354	—	288
3	355	—	—
4	339	—	256
5	340	182	280
6	357	181	278
7	355	172	—
8	347	170	259
9	356	—	274

## DISCUSSION

Considering that the diastatic activity test is essentially the measurement of a complex biochemical process, and in the light of past experiences with other types of methods for estimating the maltose produced by diastasis in flour-in-water suspensions, the Associate Referee regards the collaborative results given in Tables 1 and 2 as encouragingly satisfactory.

Special comments of individual collaborators were, with one exception distinctly favorable. There was a general tendency to give the ferricyanide method preference over other types of procedure as to convenience, reliability, simplicity, and reproduceability. A considerable number of cereal technologists are now using the method for routine mill control purposes, and they report that it meets their requirements. A few laboratories reported slightly though consistently low results. In one instance this was traced to a faulty pipet, and in another to an inaccurate thermometer in the constant temperature water bath.

The necessity for scrupulous care in matters such as the selection of pure chemicals, standardization of solutions, calibration of glassware (especially pipets), and reliable temperature control, cannot be too strongly emphasized. These matters become especially important when it is considered that a small error is multiplied many times in converting the maltose values to mg. of maltose per 10 grams of flour. With these conditions

properly controlled and insured, and with further experience in manipulation, it is believed highly probable that collaborators will reach even closer agreement than is indicated by the results here reported.

Further experience in checking among different laboratories indicates the desirability of emphasizing certain features that have apparently been factors affecting the concordance of results. (1) Some operators habitually put the 10 cc. portion of the alkaline ferricyanide solution into the test tube *first* instead of *after* the 5 cc. aliquot of the clarified flour extract. This should not be done. It has been found that more consistent and reliable values are secured by introducing the flour extract first, followed by the ferricyanide solution, as indicated in the specifications. This insures a more thorough mixing of ingredients. (2) No unnecessary time should be allowed to elapse between the addition of the KI and the titration with thiosulfate. If more than 5 or 10 minutes thus elapse, a little iodine may be lost by volatilization, especially when running blanks or samples of low reducing sugar content. In such cases the excess of ferricyanide is comparatively large, causing correspondingly greater amounts of iodine to be liberated from the KI.

It has been found that the addition of 3.8 grams of borax<sup>1</sup> to each liter of sodium thiosulfate solution will very satisfactorily stabilize the solution against deterioration, which is ordinarily a troublesome feature in handling standard thiosulfate solutions. This has been verified, and it constitutes an added convenience of considerable value.

The latest revised and improved specifications for the method, which the Associate Referee proposes for consideration as a tentative method are herewith submitted. The method has been edited to conform to the style used in *Methods of Analysis, A.O.A.C.*, and it should run under the general heading Wheat Flour.

#### DIASTATIC VALUE

##### REAGENTS

(a) *Buffer soln.*—Dissolve 6.8 g. of crystalline or 4.1 g. of *anhydrous* Na-acetate in H<sub>2</sub>O, add 3 cc. of glacial acetic acid, and dilute to 1000 cc. with H<sub>2</sub>O. The pH of this soln should be 4.6–4.8.

(b) *Sulfuric acid.*—(1+9).

(c) *Sodium tungstate soln.*—Dissolve 12 g. of Na<sub>2</sub>WO<sub>4</sub>·2H<sub>2</sub>O in H<sub>2</sub>O and dilute to 100 cc.

(d) *Alkaline ferricyanide soln.*—Dissolve 16.5 g. of pure dry K<sub>3</sub>Fe(CN)<sub>6</sub> and 22 g. of *anhydrous* Na<sub>2</sub>CO<sub>3</sub> in H<sub>2</sub>O and dilute to 1000 cc. The K<sub>3</sub>Fe(CN)<sub>6</sub> normality is 0.05. Keep in dark bottle away from light.

(e) *Sodium thiosulfate soln.*—0.05 N. Dissolve 12.41 g. of *pure* dry Na<sub>2</sub>S<sub>2</sub>O<sub>3</sub>·5H<sub>2</sub>O crystals and 3.8 g. of borax in H<sub>2</sub>O and dilute to 1000 cc. (borax prevents deterioration of the Na<sub>2</sub>S<sub>2</sub>O<sub>3</sub> soln on long standing).

(f) *Acetic acid soln.*—200 cc. of glacial acetic acid, 70 g. of KCl, and 20 g. of ZnSO<sub>4</sub>·7H<sub>2</sub>O per 1000 cc. of H<sub>2</sub>O.

<sup>1</sup> C. A., 27, 476 (1933).

(g) *Potassium iodide soln.*—To a 50% aqueous soln of freshly prepared KI add 1 or 2 drops of NaOH. (The NaOH prevents liberation of free I on standing. Soln must be colorless, indicating absence of free I.)

(h) *Soluble starch soln.*—1% in 30% NaCl soln. Suspend 1 g. of starch in a small quantity of cold H<sub>2</sub>O, and pour slowly into boiling H<sub>2</sub>O. Dissolve 30 cc. of NaCl in a small quantity of H<sub>2</sub>O. Add this mixture to the starch soln and dilute to 100 cc. with H<sub>2</sub>O.

#### STANDARDIZATION OF FERRICYANIDE AND SODIUM THIOSULFATE SOLUTION

Standardize the Na<sub>2</sub>S<sub>2</sub>O<sub>3</sub> soln. as directed under IX, 2(e), but use the quantities required for 0.05 *N* soln. Check the normality of the K<sub>3</sub>Fe(CN)<sub>6</sub> soln as follows: To 10 cc. of the K<sub>3</sub>Fe(CN)<sub>6</sub> soln add 25 cc. of the acetic acid soln, 1 cc. of the KI soln, and 2 cc. of the soluble starch soln. Titrate with the Na<sub>2</sub>S<sub>2</sub>O<sub>3</sub> soln. (It should require exactly 10 cc. of the Na<sub>2</sub>S<sub>2</sub>O<sub>3</sub> soln completely to discharge the blue starch-iodine color.)

Having prepared these solutions of specified normality, use the same simple procedure in the standardization of a new supply of either soln. at any time by merely titrating a portion of the new soln. against a portion of the previous soln. whose normality is established and known.

#### DETERMINATION

Introduce 5 g. of flour and a heaping teaspoonful of clean sand into a 100 or 125 cc. Erlenmeyer flask and *thoroughly* mix flour and sand by rotating the flask. Add 46 cc. of the buffer soln. and again mix by *rotating* the flask rapidly, until all the flour is thoroughly in suspension. Bring the flour-sand mixture and the buffer soln. *separately and individually* to 30° before combining the two. Digest the suspension for 1 hour at 30±0.2°, preferably in a water thermostat, shaking the flask (by rotation) every 15 minutes. At the end of the hour add 2 cc. of H<sub>2</sub>SO<sub>4</sub> (1+9), and mix thoroughly. Then add 2 cc. of the Na<sub>2</sub>WO<sub>4</sub>·2H<sub>2</sub>O soln., mix, and let stand 2 min. Decant through filter paper (No. 4 Whatman or its equivalent), discarding the first few drops, and pipet 5 cc. of the filtered extract into a test tube of approximately 50 cc. capacity (18–20 mm. diameter). Add 10 cc. (with pipet) of the alkaline ferricyanide soln. to the contents of the test tube, and immerse the tube in a vigorously boiling water bath to such a depth that the surface of the liquid in the test tube is 3 or 4 cm. below the surface of the boiling water. (The delay between filtration of the clarified flour extract and treatment in the boiling water bath should not exceed 15 or 20 min., due to slight tendency toward sucrose hydrolysis in acid soln.) Allow the test tube to remain in the boiling water bath for *exactly* 20 min. Immediately cool the test tube and its contents under running tap water, and pour at once into a 100 or 125 cc. Erlenmeyer flask. Rinse out the test tube with 25 cc. of the acetic acid reagent and add this to the contents of the Erlenmeyer flask, with thorough mixing. Then add 1 cc. of the KI soln. and 2 cc. of soluble starch soln. Mix thoroughly and titrate with the Na<sub>2</sub>S<sub>2</sub>O<sub>3</sub> soln. to disappearance of the blue color. (A 10 cc. buret is recommended for the Na<sub>2</sub>S<sub>2</sub>O<sub>3</sub> titration.) Subtract from 10 the number of cc. of the Na<sub>2</sub>S<sub>2</sub>O<sub>3</sub> soln. used in the titration, the difference being the number of cc. of the K<sub>3</sub>Fe(CN)<sub>6</sub> soln. reduced by the reducing sugars in the flour extract. This value is equivalent to a definite quantity of maltose, which is ascertained (in mg.) by consulting the Maltose Conversion Table. Using 5 cc. of flour extract, as specified, multiply the ascertained maltose value by 20 to give mg. of maltose per 10 grams of flour after 1 hour's diastasis.

The foregoing specifications pertain to *average* sound, normal bakers' flours, where values for mg. of maltose produced by 10 g. of flour in 1 hour will seldom ex-

ceed 340. For material giving higher values, such as products from malted or sprouted grain, use smaller portions of extract, i.e., 1, 2, or 3 cc. instead of 5 cc. In such cases, however, add enough  $H_2O$  to make up the difference in total volume, and also use a different factor for converting results into mg. of maltose per 10 g. of flour. Thus, if 2 cc. of extract is used, multiply the maltose equivalent by 50. (When the liquid in the test tube is colorless, instead of yellow, after the prescribed treatment in the boiling water bath, and gives no blue color upon the addition of  $KI$  and starch, it is apparent that there was enough reducing sugar to reduce all the  $K_3Fe(CN)_6$ , and that the determination must be repeated with a smaller quantity of extract.)

#### "BLANK" DETERMINATIONS

Two types of blank determinations may be required. One is for the purpose of detecting and making suitable correction for any impurities in the reagents having a reducing action on the  $K_3Fe(CN)_6$ . For this purpose apply the foregoing procedure to the reagents, alone, using 5 cc. of buffer soln. instead of the flour extract. If there is any appreciable reduction of the  $K_3Fe(CN)_6$ , its value can thus be measured and applied as a correction in the actual diastatic value determinations. With pure reagents this value is usually negligible. Nevertheless, it is advisable to run a blank determination of this type whenever new solutions of reagents are made up.

The other type of "blank" determination is designed to indicate the quantity of reducing sugar originally present as such, in the flour, the value for which presumably should be deducted from the total maltose value after 1 hour's diastasis. When there is assurance that the flour was milled from *sound, normal* wheat, however, this operation is, for all practical purposes, unnecessary, because the quantity of reducing sugar originally present is very small and very nearly constant, being close to 20 mg. per 10 g. of flour.

This type of blank determination need be used only when there is occasion to doubt the soundness of the flour, or in instances where there is known to have been an appreciable quantity of frosted, sprouted, or otherwise unsound or damaged kernels in the wheat from which the flour was milled. The method for this type of "blank" determination is as follows:

Add to 5 g. of flour, which has been thoroughly mixed with a teaspoonful of clean sand in a 100 or 125 cc. Erlenmeyer flask, 48 cc. of *ice cold* 0.4% (by volume)  $H_2SO_4$ . Shake thoroughly, and at once add 2 cc. of 12%  $Na_2WO_4 \cdot 2H_2O$  soln. Again mix thoroughly, and filter after 2 minutes' standing. Using 5 cc. of filtrate, proceed with the  $K_3Fe(CN)_6$  reduction method exactly as hereinbefore prescribed.

The true diastatic value of a flour is indicated by the maltose actually produced by diastasis in 1 hour under the specified conditions. To obtain this value subtract from the figure for *total maltose* per 10 g. of flour after 1 hour's diastasis the value for reducing sugar (as maltose) originally present before diastasis. As this is a constant value close to 20 mg. for 10 g. of flour, in the case of sound normal bread flours, ascertain the final diastatic value by subtracting 20 from the number of mg. of total maltose per 10 g. of flour after 1 hour's diastasis.

When it is considered necessary actually to make the blank determination, for reasons previously indicated, substitute the value found for the arbitrary value of 20, and subtract from the total maltose value after diastasis.

The maltose conversion table to be used in connection with this method will be found in *This Journal*, 16, 503 (1933).

The Associate Referee recommends<sup>1</sup> the adoption of the modified ferricyanide reduction procedure as a tentative method for the estimation of flour diastatic value.

<sup>1</sup> For report of Subcommittee C and action of the Association, see *This Journal*, 17, 68, 65 (1934).

## REPORT ON STARCH IN FLOUR

By V. E. MUNSEY (U. S. Food and Drug Administration, Washington, D. C.), *Associate Referee*

Last year the following minimum, maximum, and average results were obtained on samples of patent flour and whole wheat flour, by six collaborators: 71.36, 74.04, 72.54 and 55.02, 56.08, 55.28 per cent.<sup>1</sup> The results are good considering the large percentage of substance determined.

This year two flour samples, a very short patent and a whole wheat flour, and a copy of the same method were sent to eight collaborators. Results were received from six of the eight collaborators as follows:

ANALYST	WHOLE WHEAT FLOUR <i>per cent</i>	AVERAGE <i>per cent</i>	WHITE FLOUR <i>per cent</i>	AVERAGE <i>per cent</i>
A	57.16 57.60 57.16	57.31	77.36 77.32	77.34
B	57.84 57.85	57.85	77.82 77.26 77.52	77.53
C	57.26 57.88	57.57	78.52 78.00	78.26
D		56.04		78.56
E	56.30 56.34	56.32	76.38 75.80 75.66 75.80	75.91
F	—	—	74.74 74.70 75.10	75.85
Min.		56.04		74.85
Max.		57.85		78.56
Av.		57.14		76.70

These results are not entirely satisfactory, but the method is not so hopeless as these results indicate. Last year the results were better, and some of the chemists have consistently reported good results. This method is strictly empirical; every step in the procedure must be followed in detail. The analyst will realize the importance of this precaution when consideration is given to the principle of the method. It is well known that the starch particles are surrounded by cell walls. Therefore, the macera-

<sup>1</sup> *This Journal*, 16, 504 (1933).

tion should be sufficiently complete and the acid treatment sufficiently long to disperse all the starch in the hydrochloric acid solution. Such acid treatment should disperse all the starch in the hydrochloric acid solution, but at the same time the analyst should guard against too high a temperature or too long an acid treatment as in each case low results will follow. These precautions regarding temperature and length of acid treatment should be particularly kept in mind until the precipitation of the starch in the alcohol.

This method is specific for starch, it is short, simple, and, in the opinion of the Associate Referee, capable of giving satisfactory results when the analyst is familiar with the procedure. Accordingly, it is recommended<sup>1</sup> that the modified Rask method<sup>2</sup> for the determination of starch be made tentative.

## REPORT ON FLOUR-BLEACHING CHEMICALS

By DOROTHY B. SCOTT (U. S. Food and Drug Administration,  
New York, N. Y.), *Associate Referee*

During the past year J. L. Hogan of the New York Station has used with satisfactory results on 68 samples of flour the modification of the tentative quantitative method (*Methods of Analysis, A.O.A.C.*, 1930, 173, 39) proposed by the Associate Referee for the determination of chlorine in bleached flour.

However, when a study was made on the same flour with the proposed method and the method of Kent-Jones and Herd [*J. Soc. Chem. Ind.*, **49**, 223T (1930)], he was unable to check when large quantities of chlorine were present. Much more chlorine was obtained by the modified Rask method than by the Kent-Jones and Herd method. Sufficient silver nitrate was always added to allow for the quantity of chlorine in the sample.

The results of these few experiments obtained by Hogan follow:

### *Chlorine—Modified Rask Method Kent-Jones and Herd Method*

<i>mg. per kilo</i>	<i>mg. per kilo</i>
—	2.9
2.4	2.4
14.4	5.3
14.4	
4.4	1.0
4.4	0.8
28.0	12.0
25.2	11.7
21.1	5.7
20.3	6.3

<sup>1</sup> For report of Subcommittee C and action of the Association, see *This Journal*, 17, 58 (1934).

<sup>2</sup> *This Journal*, 16, 504 (1933).



The New York Station will continue to study the two methods and endeavor to determine the cause of the discrepancy when large quantities of chlorine are present.

Samples of flour were sent out for collaborative study of the Associate Referee's method for the detection of benzoyl peroxide as benzoic acid in flour. As the results have been slow in coming in, the data will be published at a later date [see *This Journal*, 17, 302 (1934)].

It is recommended<sup>1</sup>—

(1) That methods for the determination of chlorine in bleached flour be studied further.

(2) That the method of the associate referee for the detection of benzoyl peroxide as benzoic acid be studied further.

No report on foreign methods for testing flours was given by the associate referee.

No report on CO<sub>2</sub> in self-rising flour was given by the associate referee.

## REPORT ON SAMPLING AND DETERMINATION OF MOISTURE IN ALIMENTARY PASTE, BREAD, AND BAKED PRODUCTS

By L. H. BAILEY (Bureau of Chemistry and Soils,  
Washington, D. C.), *Associate Referee*

### MOISTURE

A collaborative study was made for the purpose of securing additional data on the determination of moisture in air-dried baked products other than bread. The samples tested this year were fig bars and soda crackers. Three collaborators made moisture determinations by both the vacuum oven and the 130°C. air oven methods. In some instances the analyst did not make the determination by the air oven at the same time that he did by the vacuum oven. This fact may account for some of the discrepancies in the results by the two methods.

The material of the fig bars, is not of uniform composition, and there is no way of getting it subdivided so as to have an equal distribution of fig paste and flour material throughout the comminuted mass. The collaborative results are shown in the table.

In the case of the soda crackers closely agreeing duplicates were obtained in every case, and two of the three analysts secured practically the same results by the two methods. It is considered that both of these meth-

<sup>1</sup> For report of Subcommittee C and action of the Association, see *This Journal*, 17, 58 (1934).

*Moisture in baked products*

COLLABORATOR	Vacuum Oven Method		130°C. Air Oven Method	
	FIG BARS per cent	SODA CRACKERS per cent	FIG BARS per cent	SODA CRACKERS per cent
R. G. Capen	13.49	9.75	13.23	9.66
	13.39	9.73	13.52	9.67
Gordon Smith	13.93	9.97	11.26	9.46
	14.43	10.06	11.50	9.46
L. H. Bailey	12.47	9.50	11.69	9.49
	12.52	9.57	12.46	9.53
	12.00		11.99	
	12.19		11.52	

ods are satisfactory, and either one may be used to determine moisture in any air-dried baked product that has a uniform composition and can be ground or pulverized into a homogeneous mass. On the other hand, if the product is not of uniform composition (fig bars, fruit cake, raisin cookies, etc.) it is necessary to subdivide the product as finely as is practicable and then either take much larger portions or a larger number of replicate portions for the determination of moisture.

## SAMPLING

The Associate Referee gave consideration to the subject of sampling and conferred with regulatory officials. The present tentative method is a practical working method and will be found satisfactory for use in most cases, but for some particular investigation it may be necessary to modify the method to meet the needs of the special inquiry. For this reason it is considered desirable to allow this method to remain as tentative, and it is so recommended.

RECOMMENDATIONS<sup>1</sup>

It is recommended—

(1) That the vacuum oven method be made official for the determination of moisture in all air-dried baked products not containing fruit (final action).

(2) That the 130°C. air oven method be made official for the determination of moisture in all air-dried baked products not containing fruit (final action).

(3) That a foot-note be appended to both methods of determining moisture, stating the necessity of using either an unusually large portion or several small portions in order to have a representative sample for the determination of moisture in such samples as fig bars, fruit cake, raisin cookies, etc.

(4) That the method for preparation of sample—alimentary paste—be retained as a tentative method.

<sup>1</sup> For report of Subcommittee C and action of the Association, see *This Journal*, 17, 59 (1934).

No report on unsaponifiable matter in alimentary paste, bread, and baked products was given by the associate referee.

No report on lipoids, lipid  $P_2O_5$  fat, and crude albumin nitrogen in alimentary paste, bread, and baked products was given by the associate referee.

## REPORT ON CRUDE FIBER IN BAKED PRODUCTS

By R. G. CAPEN (Bureau of Chemistry and Soils,  
Washington, D. C.), *Associate Referee*

The method for the determination of crude fiber in baked products was further studied, and special attention was given to the official method under Grain and Stock Feeds (*Method of Analysis A.O.A.C.*, 1930, 280).

Samples of soda crackers and fig newtons were used in the collaborative work. Owing to their gumminess, it was necessary to dry the fig newtons before they could be satisfactorily ground. It was also necessary to grind the seeds thoroughly, otherwise high results were obtained.

Two gram samples were taken in all cases. The results of the collaborators checked very closely in the case of the crackers; in the case of the fig newtons there was a slight variation due to the nature of the sample.

<i>Collaborative results</i>			
	(1)	(2)	(3)
	<i>per cent</i>	<i>per cent</i>	<i>per cent</i>
Fig newtons	0.79 } 0.96 } 0.87	1.24 } 1.05 } 1.15	0.92 } 1.02 } 0.96
Soda crackers	0.24 } 0.24 } 0.24	0.26 } 0.24 } 0.25	0.27 } 0.22 } 0.25

It is recommended<sup>1</sup> that the method for the determination of crude fiber in baked products be made official (first action).

A paper entitled "Problems of Interest in the Baking Industry" was presented by C. B. Morison, Chicago, Ill. An abstract of this paper was published in *Cereal Chemistry*, 11, 100 (1934).

## REPORT ON MILK SOLIDS IN BREAD

By ARNOLD H. JOHNSON (1403 Eutaw Place,  
Baltimore, Md.), *Associate Referee*

The work on the estimation of milk in bread was continued, one of the procedures outlined last year being followed. The procedure that ap-

<sup>1</sup> For report of Subcommittee C and action of the Association, see *This Journal*, 17, 59 (1934).

peared to be the most promising was to determine the lactose and then calculate the total milk solids of the bread from the lactose content.

The interior of the loaf was removed and dried. The dried bread was ground, and a weighed portion was extracted with ether to remove fat. Sugars other than lactose were fermented away with yeast. The yeast, flour protein, and other suspended matter were then precipitated by the phosphotungstate method, and a clear filtrate was obtained. The lactose content of the clear filtrate was determined by the use of Fehlings solution.

The method suggested has been found to give fairly satisfactory results, but there are certain details to be worked out. It is recommended that the work be continued.<sup>1</sup>

## REPORT ON RYE IN FLOUR MIXTURES

By J. H. BORNMAN (U. S. Food and Drug Administration,  
Chicago, Ill.), *Associate Referee*

Subcommittee C adopted the suggestion of the Associate Referee that the tests proposed for the detection of rye flour in wheat flour and bread be studied collaboratively. The tests proposed were the modified Tillmans method, the König-Bartschat method, and the chloroform test.

Owing to lack of time, the work this year was restricted to a collaborative study of the modified Tillmans method and of the chloroform test.

The following samples sent to collaborators: No. 1—Wheat Flour, No. 2—Rye Flour, No. 3—10 per cent Rye Flour (from Nos. 1 and 2), No. 4—20 per cent Rye Flour (from Nos. 1 and 2), and No. 5—Rye Bread, were to be used in testing the Tillmans method. The following five samples of flour were used for the chloroform test: A—Pure Wheat Flour, B—20 per cent Rye Flour, C—15 per cent Rye Flour, D—10 per cent Rye Flour, and E—5 per cent Rye Flour.

It was planned to use the Strohecker<sup>2</sup> modification of the Tillmans method. A trial, however, showed that filtration was extremely slow in the case of a water extract of rye flour. By using approximately 70 per cent alcohol for the extraction, the filtration was reasonably rapid. This alteration amounts to combining two steps of the Strohecker procedure into one. It may be mentioned that the modification of Kruisheer<sup>3</sup> also makes use of 70 per cent alcohol to extract the trifufructosan from the flour.

### MODIFIED TILLMANS METHOD

(For the estimation of rye flour in mixed flour and bread)

Introduce 2.50 grams of the sample into a 100 cc. volumetric flask. Add 25 cc. of water and shake well until smooth and free from lumps. Add sufficient dialyzed

<sup>1</sup> For report of Subcommittee C and action of the Association, see *This Journal*, 17, 59 (1934).

<sup>2</sup> *Z. Unters. Lebensm.*, 63, 514 (1932).

<sup>3</sup> *Rec. trav. chim.*, 50, 153 (1931).

iron solution to give a yellow tint to the supernatant liquid (not over 1.25 cc.) and shake well. Dilute to the mark with 95% alcohol, shake, and re-dilute to the mark if there has been a contraction in volume. Allow to stand 10 minutes.

Filter into a 50 cc. glass-stoppered cylindrical graduate, collecting exactly 45 cc. of filtrate. Add 5 cc. of 0.5 *N* alcoholic KOH by means of a pipet, and shake well. Filter promptly on a Gooch crucible and wash cylinder and crucible with two 5 cc. portions of 95% alcohol. Place a test tube of 30 cc. capacity in the filter flask and wash the precipitate from the Gooch crucible with three 25 cc. portions of hot water, pouring the filtrate from the test tube into the cylinder in which the precipitation took place, and from the cylinder into a 100 cc. volumetric flask. Invert by the rapid method (69°–70°C.) and determine the reducing value on 50 cc. by the Munson and Walker method.

The chloroform test has been published.<sup>1</sup>

TABLE 1.—*Chloroform test for rye flour*

COLLABORATOR	<sup>A</sup> WHEAT	<sup>B</sup> 20% RYE	<sup>C</sup> 15% RYE	<sup>D</sup> 10% RYE	<sup>E</sup> 5% RYE
L. H. Bailey Bur. Chem. & Soils	Negative	Positive	Positive	Positive	Negative?
George Garnatz Kroger Food Founda- tion	Negative	Positive	Positive	Positive	Positive
H. C. Gore Fleischmann Labora- tories	Negative	Positive	Positive	Positive	Negative
M. Harris Chicago Sta.	Negative	Positive	Positive	Positive	Positive
Gordon Smith Food Control	Negative	Positive	Positive	Positive	Positive
Carl B. Stone Minneapolis Sta.	Negative	Positive	Positive	Positive	Negative
M. J. Gnagy New Orleans Sta.	Negative	Positive	Positive	Positive	Positive

#### COMMENTS OF COLLABORATORS

*L. H. Bailey.*—With Sample E it was difficult to decide from the test whether or not any rye was present, therefore I marked it negative. I do not know whether the unsatisfactory checks on Nos. 3 and 5 were due to incomplete removal of the sugar by washing with 75 cc. of hot water, or from some other cause. Regarding the application of the method for determining the amount of rye in rye bread, it seems from my results that the method is entirely worthless. I obtained less cuprous oxide from the bread than from white flour alone.

*George Garnatz.*—We are favorably impressed with the chloroform test.

Samples 1 to 5 were used in connection with the modified Tillmans method, and duplicate determinations were run on two occasions after a lapse of two weeks. The first analysis gave apparently good checks and fair results which led us to be favorably impressed with the method, but upon repeating the analyses after two weeks, we obtained unsatisfactory replication. It is possible that during the two

<sup>1</sup> *This Journal*, 17, 85 (1934).

TABLE 2.—*Estimation of rye flour from reducing value by modified Tillmans method*

COLLABORATOR	1 PURE WHEAT	2 PURE RYE	3 10% RYE	3 RYE ESTIMATED	4 20% RYE	4 RYE ESTIMATED	5 RYE BREAD
	Mg. Cu <sub>2</sub> O	Mg. Cu <sub>2</sub> O	Mg. Cu <sub>2</sub> O	per cent	Mg. Cu <sub>2</sub> O	per cent	Mg. Cu <sub>2</sub> O
L. H. Bailey	4.6	24.0	10.2	20	10.2	30	3.6
	5.0	24.0	7.2		10.8		5.2
J. H. Bornmann	9.9	27.2	11.5	9	11.9	12	4.7
George Garnatz	7.8	23.4	7.5	0	10.9	21.3	2.8
	7.4	22.8	8.3	4.5	11.8	24.5	3.1
	3.6	23.5	1.1	0	8.4	23.4	2.2
	3.1	23.1	6.1	11.6	7.3	17.9	3.7
H. C. Gore	4.0	22.0	4.0	11	12.0	40	4.0
		21.0	8.0		10.0		
Gordon Smith	14.0	23.4	15.4	15	12.3	0	10.8
Carl B. Stone	10.4	24.3	9.1	0	11.0	9	5.5
	10.3	25.9	10.2		10.3		5.6
	9.7		9.3		12.3		6.0
			9.2				
M. J. Gnagy	23.5	40.5	29.5	30*	17.5	13*	15.7
	23.3	(28.3)	25.6		20.8		17.7
	20.7	33.4	20.0		22.9		8.6
	11.6	34.8	19.6		20.3		
	10.5	33.7					

\* Calculated by Associate Referee from average values.

weeks which elapsed between the first and second analyses there was some change in the dialyzed iron solution.

We have two definite objections to the method, namely, the carbohydrates precipitated by the alcoholic potassium hydroxide solution so clog the asbestos filter that not only is considerable time required for filtration and washing, but completeness of these steps seems almost impossible. In addition, the amount of cuprous oxide formed is too small to attain any great degree of accuracy. This is apparent from the number of grams of cuprous oxide that are obtained for weighing.

*H. C. Gore.*—I found the modified method to be laborious and time-consuming. It is not very exact since the error of the Munson and Walker method, under the best of operating conditions, is of the order of  $\pm 1$  mg.

*C. B. Stone.*—The results secured on the different samples do not give close checks. Perhaps this is due to the analyst or the method. The amount of cuprous oxide found in Samples 3 and 4 does not show a wide enough variation from Sample 1 to give very conclusive results that Samples 3 and 4 are mixtures. Why should Sample 5 give such low results if it is a rye bread?

*M. J. Gnagy.*—I regret to say that the results I obtained by the modified Tillmans method are far from satisfactory. Trouble was encountered in retaining the cuprous oxide upon the Gooch crucible because of the extremely fine nature of the

precipitate. Cuprous oxide was known to have been lost in one determination, and loss was suspected in others. This was believed to have been overcome by using special care in preparing the crucibles used later.

Trouble was also encountered in filtering after the addition of some of the second lot of dialyzed iron in the case of No. 1 wheat flour. Three attempts were abandoned before results were secured. The amount added was cut down. It is believed that the second lot of dialyzed iron was more concentrated than the first, as the first lot received had considerable sediment in the bottom of the bottle. No trouble was encountered in filtering in the case of the other samples.

From the results obtained, it is impossible to calculate the relative proportions of wheat flour and rye flour in the mixtures, however I should not wish to condemn the method entirely.

### DISCUSSION OF RESULTS

Table 1 shows the results of collaborators with the chloroform test. All results are correct except three on Sample E, which was 5 per cent rye. This would seem to indicate that 5 per cent is in the doubtful zone. As the standards for wheat permit 7 per cent of rye, it might be possible to have a legal wheat flour containing 5 per cent of rye flour. In view of this fact it is hardly to be regretted if the chloroform test does not detect the presence of 5 per cent rye. A definitely positive test will probably indicate the presence of an appreciable amount of added rye flour. It should be pointed out that the tests in this case were made on mixtures of the flours which served as known samples. The method should be tried out on a larger number of samples from widely different points of origin.

The results on the modified Tillmans method are far from satisfactory. The difficulty appears to be due to the fact that the amount of reducing sugar determined in most cases is too small. If the procedure can be altered so as to obtain a sufficiently concentrated extract of trifructosan the experimental error in the Munson and Walker method will be negligible. The objection of some collaborators that filtration is slow may be obviated by using the correct amount of dialyzed iron. It will, of course, be necessary to accumulate data on a number of samples of known composition for use with this method. Furthermore, it will be necessary to have a separate set of data for bread since some of the trifructosan is destroyed in the baking process. It is felt that the method has sufficient merit to warrant further work.

### RECOMMENDATIONS

It is recommended<sup>1</sup>—

- (1) That the chloroform test be adopted tentatively as a test for rye in flour.
- (2) That the chloroform test, the modified Tillmans method, and the König-Bartschat method be further studied.

<sup>1</sup> For report of Subcommittee C and action of the Association, see *This Journal*, 17, 58, 65 (1934).

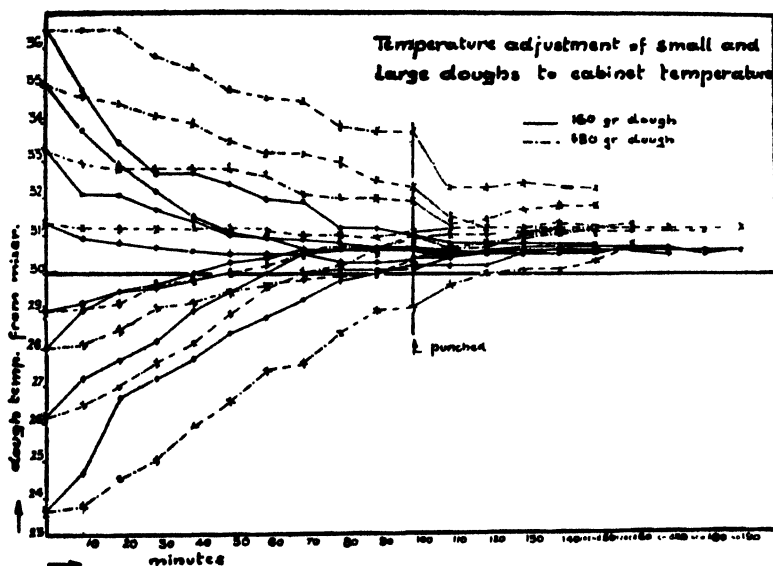
## REPORT ON EXPERIMENTAL BAKING TEST

By E. MUNZ and C. G. HARREL, *Associate Referee* (Pillsbury Flour Mills Co., Minneapolis, Minn.)

## I. IMPORTANCE OF DOUGH TEMPERATURE

In their conclusions and recommendations as to the basic procedure for the experimental baking test, Merritt, Blish, and Sandstedt<sup>1</sup> state that the temperature of the water should be such that doughs come from the mixing operation at  $30 \pm 2^\circ\text{C}$ .

C. G. Harrel<sup>2</sup> points out that in commercial experience a variation of  $\pm 2^\circ\text{C}$ . is too large and that the temperature range should be limited to  $30 \pm 0.5^\circ\text{C}$ .



GRAPH I

A. E. Treloar and R. K. Larmour<sup>3</sup> did not find any correlation between the initial dough temperature and the loaf volume, provided the dough temperature was kept within the range of  $30 \pm 2^\circ\text{C}$ .

Harrel's conclusion as to the importance of dough temperature was mainly based on experience in commercial bakeshops, where the temperature limit is  $80^\circ \pm 1^\circ\text{F}$ . and greater variations are not tolerated. Treloar and Larmour suggested that the importance of the deviation of temperature is related to dough size.

In order to secure definite data on this subject, the writers determined

<sup>1</sup> *Cereal Chem.*, 9, 175 (1932).

<sup>2</sup> *Ibid.*, 10, 165 (1933).

<sup>3</sup> *Ibid.*, 8, 95 (1931).



the march of temperature in 160 gram and 480 gram doughs of different initial temperature when placed in a cabinet at  $30 \pm 0.2^\circ\text{C}$ . The cabinet used was designed by C. H. Bailey.<sup>1</sup> The thermometers, which previously had been calibrated, were placed in the center of the doughs, and the temperature was read at 10 minute intervals. The data are plotted in Graph I.

The most interesting fact established in this series of temperature determinations is that the equilibrium temperature of a 160 gram dough is about  $0.5\text{--}0.8^\circ\text{C}$ . and of a 480 gram dough about  $1.0\text{--}1.4^\circ\text{C}$ . above the cabinet temperature. In the 480 gram dough, the equilibrium temperature is attained much more slowly and the range seems to be somewhat wider than with small doughs. It is therefore advisable that the cabinet temperature be set about  $0.6^\circ\text{C}$ . below the desired fermentation temperature for "pup" loaf doughs and about  $1.2^\circ$  below for pound loaf doughs. This temperature elevation is brought about by the heat of reaction of the fermentation process. The larger dough, having less surface in proportion to the volume, naturally establishes a higher equilibrium temperature.

With a variation of  $\pm 2.0^\circ\text{C}$ . from equilibrium temperature, about 40 minutes for the 160 gram doughs and about 90–100 minutes for 480 gram doughs are necessary to bring the temperature of the doughs within  $\pm 0.5^\circ\text{C}$ . of the equilibrium temperature. It is expected that the large doughs handled in commercial bakeshops stay at practically the temperature at which they come out of the mixer or that the temperature even increases in case the shop temperature is about the same as the dough temperature.

After they have been divided, the doughs stay only 20 minutes in the overhead proofer, which time period is too short for the pound loaf doughs to become adjusted to shop temperature. Hence the importance of keeping the dough temperature within narrow limits in the commercial bake-shop.

Table 1 gives the baking results from the doughs mixed at varying temperatures. The mixing was done in a Fleischmann laboratory mixer, otherwise the A.A.C.C. basic procedure was strictly followed. Four hundred grams of flour was mixed, and the dough was divided into 160 gram and 480 gram portions. After fermentation, the 480 gram dough was divided into three pieces and baked at the same time as the 160 gram dough. The volume given in the table is the average of the three loaves from the 480 gram dough.

Although the temperature adjusts itself much more slowly in the 480 gram dough, no consistently significant difference was observed in the finished bread. This is in agreement with the findings of Treloar and

<sup>1</sup> *Cereal Chem.*, 7, 341 (1930)



Larmour, and therefore the writers feel justified in stating that in the "pup" loaf baking test, a temperature variation of  $\pm 2^{\circ}\text{C}$ . in the dough coming from the mixer has no consistent measurable effect on the finished loaf.

## II. IMPORTANCE OF SPECIFICATION OF YEAST

Merritt, Blish and Sandstedt<sup>1</sup> state that "modern bakers' yeast seems to be reasonably uniform and its degree of freshness is not a critical factor, as is generally assumed." Harrel<sup>2</sup> criticized this statement, pointing out that some localities are not in the fortunate position of receiving properly transported yeast and that the proper specifications about yeast delivery and storage should be given.

Experimental data about storage conditions of yeast are numerous. Neumann<sup>3</sup> states that "Yeast loses about half of its fermenting power when stored at  $20^{\circ}$ – $23^{\circ}\text{C}$ . for 3 days. At lower temperature, however, ( $6^{\circ}$ – $7^{\circ}\text{C}$ .) yeast increases its fermenting power and even after 17 days is in better condition than at the beginning of the experiment. Too cold a room is not recommended because the sudden temperature change of the yeast when used may easily be harmful."

Larmour and Brockington<sup>4</sup> found that "between 7 and 19 days, yeast stored on ice undergoes no change in rate or amount of  $\text{CO}_2$  production, neither is there any significant difference in baking results. Thereafter the loaf volume increases until the yeast reaches an age of 30 to 33 days, at which time it decreases, but the value never becomes so low as the value obtained with 7-day-old yeast. The rate of  $\text{CO}_2$  production in dough is quite constant up to an age of 26 days but thereafter it increases somewhat and maintains a higher though more irregular level until an age of 56 days is attained by the yeast."

As Larmour and Brockington did not carry out any comparisons between yeast stored at  $0^{\circ}$  and  $6^{\circ}$ – $7^{\circ}\text{C}$ ., the writers cannot say definitely whether there is justification for Neumann's statement that excessively cold storage is not recommended because of the sudden temperature change when the dough is removed from the storage to the baking room.

Herman and Hart<sup>5</sup> stored yeast for 3 days at  $18^{\circ}\text{C}$ . without noting any deleterious effect. Staiger and Glaubitz<sup>6</sup> froze yeast at  $-10^{\circ}$  to  $-25^{\circ}\text{C}$ . from 1 to 5 days and thawed it out for 24 hours at room temperature and at  $5^{\circ}\text{C}$ . without observing any effect on the baking quality.

As a safeguard against improper delivery and storage of yeast, the following specification is recommended: "Fresh yeast is yeast that is delivered at a temperature not higher than  $15^{\circ}\text{C}$ . and stored at temperatures

<sup>1</sup> *Cereal Chem.*, 9, 235 (1932).

<sup>2</sup> *Ibid.*, 10, 165 (1933).

<sup>3</sup> *Brotrgetreide und Brot*, p. 147. Verlagsbuchhandlung Paul Parey, Berlin (1929).

<sup>4</sup> *Canadian J. Research*, 6, 614 (1932).

<sup>5</sup> *Cereal Chem.*, 4, 157 (1927).

<sup>6</sup> *Z. Spiritusind.*, 52, 116 (1929).

not higher than 10°C. for periods not longer than two weeks." These specifications do not assure uniform yeast, but they at least guard against harmful storage conditions.

A factor which oftentimes is not given due consideration is the difference between yeast brands or strains. Werner and Siedhoff<sup>1</sup> differentiated between faster and slower working strains of yeast by changing the sugar content of the baking formula. They called the formula containing 5 per cent sugar the "positive bake" and that containing 2½ per cent sugar the "negative bake." A fast-working yeast would show up badly in the negative bake and would be good in the positive bake, while the reverse would be true of a slow-working yeast.

Jørgensen<sup>2</sup> showed that loaf volume obtained by the A.A.C.C. basic method varies according to whether a slow or fast-working yeast is used. Herman and Hart<sup>3</sup> did not find any appreciable differences in the finished loaves in which two commercial brands of yeasts (E and D) had been used. They state, however, that the height of the E doughs was consistently two-thirds of the height of the D doughs at the first punch, while the height in the pan following proofing was practically identical. It seems therefore quite possible that in the case of the D doughs there was already some starvation of the yeast when proofed with consequent lower gas production, and therefore the E doughs happened to proof with about the same speed as the D doughs.

Cook and Malloch<sup>4</sup> found great differences in the gas production of two commercial yeasts; in one case the gas production of one of the yeasts was twice that of the other.

It can be stated generally that all available data show that different yeasts vary considerably in their gas-producing ability. No conclusive data have been found, however, showing to what extent different yeasts affect dough properties and dough development. As this is a very important point in the question of yeast standardization, an attempt was made by the writers to throw some light on the subject.

Three leading yeast brands (1, 2, and 3) were used. All yeast samples were properly delivered and stored. The A.A.C.C. baking method<sup>5</sup> was adhered to with the exception that the doughs were mixed in a Fleischmann laboratory mixer. In the case of the patent flours (a spring wheat of 12.2 per cent protein and 0.44 per cent ash, and a Southwestern winter wheat of 11.2 per cent protein and 0.40 per cent ash) 2 and 3 hours were chosen for fermentation time, while on the clear (spring wheat clear, 15.0 per cent protein and 0.75 per cent ash) the fermentation time was 3 and 4 hours.

The results are given in Table 2 (all data are the average of duplicate

<sup>1</sup> *Cereal Chem.*, 6, 196 (1929).

<sup>2</sup> *Ibid.*, 8, 361 (1931).

<sup>3</sup> *Loc. cit.*

<sup>4</sup> *Cereal Chem.*, 7, 133 (1930).

TABLE 2.—Comparison of commercial yeasts

FLOUR	FERM. PERM. TIME	ABS. per cent	LOAF VOLUME			GRAIN			TEXTURE			BREAK		
			NO. 1	NO. 2	NO. 3	NO. 1	NO. 2	NO. 3	NO. 1	NO. 2	NO. 3	NO. 1	NO. 2	NO. 3
			cc.	cc.	cc.									
Winter wheat (South-west) patent Protein 11.3% Ash 0.40%	hours	min.												
	2	2	65	470	500	480	6	7½	7	7	8	7	8	R
	3	2	65	460	490	490	8	8	8	9	8	8	R	R
	2	2½	63	470	515	515	7	7½	7	7	8	8	I	R
Spring wheat (North-west) patent Protein 12.2% Ash 0.44%	3	2½	63	460	510	510	6	9	9	7	9	8½	I	R
	2	3	64	490	485	525	7	6	8	8	6½	8½	M	M
	3	3	64	490	490	500	8½	7½	8	8½	7½	8	M	M
	3	4	69	590	570	610	4	4½	4	7	7	7	M	M
Spring wheat clear Protein 15.0% Ash 0.75%	4	4	69	530	530	537	4½	4½	5	7	7	7	M	M
	2	1	63	485	495	527	8	8	9	8	8½	9	R-T	R-M
	3	1	63	480	500	540	8	8	8½	7½	9	8½	T	R-T
	2	2	66	503	515	535	7	7½	8	7	8½	8½	R	M
Winter wheat (South-west) patent Protein 11.30% Ash 0.40%	3	2	66	500	510	530	8	8	8½	8½	8	8½	T	R-T
	2	2	65	490	510	557	6½	6½	6	7½	7½	7	N	I-M
	3	2	65	480	480	520	5½	6	5	7	6	6½	I-M	I-M
	3	2	65	480	480	520	5½	6	5	7	6	6½	I-M	I-M

\* Break: R Ragged; T Torn; I Incomplete; M Medium; N No break; B Badly.

TABLE 3.—*Differences in baking data in each series*  
(Obtained by subtracting the lowest value from each of the other two in the series. The data are divided into two major groups according to fermentation time.)

FLOUR TYPE	FERM. TIME	MIXING TIME	ABS.	LOAF VOL.			GRAIN			TEXTURE			DOUGH DEVELOPMENT
				NO. 1		NO. 2	NO. 1		NO. 2	NO. 1		NO. 2	
				cc.	cc.	cc.	NO. 1	NO. 2	NO. 3	NO. 1	NO. 2	NO. 3	
Winter wheat patent	hours	min.	percent										
	2	2	65	0	30	10	0	1½	1	0	1	0	Properly dev.
	2	2½	63	0	45	45	0	½	0	0	1	1	Not properly dev.
	2	1	63	0	10	42	0	0	1	0	½	1	Not properly dev.
Spring wheat patent	2	2	65	0	12	32	0	½	1	0	1½	1½	Properly dev.
	2	3	64	5	0	40	1	0	2	1½	0	2	
	2	2	65	0	20	67	½	½	0	½	½	0	
	3	4	69	20	0	40	0	½	0	0	0	0	
Average				3	17	40	.2	.5	.7	.3	.8	.8	
Winter wheat patent	3	2	65	0	30	30	0	0	0	1	0	0	Properly dev.
	3	2½	63	0	50	50	0	3	3	0	2	1½	Not properly dev.
	3	1	63	0	20	60	0	0	½	0	1½	1	Not properly dev.
	3	2	66	0	10	30	0	0	½	½	0	½	Properly dev.
Spring wheat patent	3	3	64	0	0	10	1	0	½	1	0	½	Properly dev.
	3	2	65	0	0	40	½	1	0	1	0	½	Not properly dev.
Clear	4	4	69	0	0	7	0	0	½	0	0	0	Properly dev.
Average				0	16	32	.5	.6	.7	.5	.5	.6	

SHORT FERMENTATION

LONG FERMENTATION

TABLE 4.—*Doughs proofed to standard height*

FLOUR	MIXING TIME	ABR.	FERM. TIME	PROOF-TIME			VOLUME			GRAIN			TEXTURE			BREAK		
				NO. 1	NO. 2	NO. 3	NO. 1	NO. 2	NO. 3	NO. 1	NO. 2	NO. 3	NO. 1	NO. 2	NO. 3	NO. 1	NO. 2	NO. 3
				min.	per cent	hours	cc.	cc.	cc.									
S. W. Win- ter Patent Prot. 11.2%	1	63	2	57	59	59	480	510	518	6½	7½	7½	8	9½	7½	BT	R	R
	1	63	3	66	72	61	497	522	547	7½	8	8½	8½	8	9	BT	T	R

results). In Table 3 are complete computations of the excess volumes or points over the lowest result in the series. The conclusions from these experiments follow.

Different yeast brands are not only different in their gas-producing ability but they also produce doughs of different smoothness and gas-retaining capacity. This was more apparent on the weaker Southwestern winter wheat flour, especially when this flour had not been properly developed in the mixing operation. Properly developed dough is understood by the writers to be a dough whose absorption and mixing time have been so adjusted that optimum baking results with the particular flour are obtained after 3 hours of fermentation.

It was observed, especially on the doughs from the Southwestern flours that were somewhat on the stiffer side, that yeasts Nos. 2 and 3 produced a much smoother dough during fermentation. The dough from yeast No. 1 started to tear in the proof and had very little oven spring. In order to obtain a more precise picture of the extent to which the differences between the loaves are due to gas production or dough properties, the doughs were proofed up to standard height. In this case, the volume is a good measure for oven spring or gas-retaining capacity of the dough (Table 4).

The differences are practically of the same magnitude as before, leaving little doubt that the effect of different yeast on dough properties is very pronounced. The variation in one and the same yeast brand has not been particularly studied. Herman and Hart found significant variation in the gas production of one yeast brand and less in another yeast brand.

The data also show some variation in one brand (Table 5). The method used was essentially that described by Blish<sup>1</sup> for the determination of the "gassing power" of a flour, but instead of flour 60 mg. of sucrose was used.

To what extent these variations will affect

<sup>1</sup> *Cereal Chem.*, 9, 378 (1932).

the baking test is not known. The opinion of the writers is that the variation in one particular brand is not nearly so serious as the differences between brands.

TABLE 5.—*Daily variations in gassing power of a single brand of yeast*  
(Data are recorded in mm. Hg. pressure)

TEST	DAYS									
	1ST	2ND	3RD	4TH	5TH	6TH	7TH	8TH	9TH	10TH
1st	123	106	118	102	102	107	114	106	112	123
2nd	123	118	116	102	107	100	113	102		

The present investigation shows again the difficulty of a standardization of the baking test. The standpoint of Kent-Jones and others, that efforts should be made to standardize the physical methods and adjust the baking test more to individual conditions seems very well justified.

## SUMMARY AND CONCLUSIONS

### *Dough temperature*

1. The findings of Merritt, Blish and Sandstedt; Treloar and Larmour, and others—that a temperature range of  $30 \pm 2.0^{\circ}\text{C}.$  of the dough coming from the mixer is of no measurable influence on the “pup” loaf baking test—are confirmed.

2. The adjustment of a 160 gram dough to the cabinet temperature proceeds much faster than that of a 480 gram dough. When the temperature of the dough coming from the mixer varies  $\pm 2.0^{\circ}$  from the equilibrium temperature about 40 minutes is necessary for a 160 gram dough and 90–100 minutes for a 480 gram dough to bring the temperature of the dough within  $\pm 0.5^{\circ}\text{C}.$  of the equilibrium temperature.

3. The equilibrium temperature in a 160 gram dough is  $0.5\text{--}0.8^{\circ}\text{C}.$  above the cabinet temperature ( $30^{\circ}\text{C}.$ ); that of a 480 gram dough is somewhat higher ( $1.0\text{--}1.5^{\circ}\text{C}.$ ).

4. For the “pup” loaf baking test, it is recommended that the fermentation cabinet temperature be set at  $29.5^{\circ}$  in order to assure a dough temperature of  $30^{\circ}\text{C}.$

### *Yeast variability*

1. Yeast can be stored for 2–3 weeks without any deleterious effect, provided it is guarded against higher temperature. As a safeguard against improper delivery and storage of yeast, the following specifications are recommended: By “fresh” yeast is meant yeast that is delivered at a temperature not higher than  $15^{\circ}\text{C}.$  and stored at a temperature not higher than  $10^{\circ}\text{C}.$  for a period not longer than 2 weeks.

2. Great differences exist in yeasts of different brands or strains in regard to gas produced as well as effect on dough properties.



3. The differences in regard to dough properties are largest in weaker flours and in doughs which are not properly developed in the mixing operation.

4. Specifications for yeast in regard to gas production and influence on dough properties cannot be made, as different flours are not affected alike.

5. It is therefore recommended<sup>1</sup> that the suggestion made by Cook and Malloch (1930)—that arrangements be made with a yeast company to place a special yeast for experimental purposes on the market—be further studied.

#### ACKNOWLEDGMENT

The Associate Referee on Experimental Baking Test wishes to express thanks to Emil Munz for conducting the experimental work herein reported, and both the writers desire to acknowledge the facilities of the University of Minnesota where the majority of the baking tests were conducted, and to thank C. L. Brooke for help rendered.

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A paper, entitled "Enzymes of Flour in Relation to Yeast Fermentation," was presented by Charles N. Frey, New York City. This paper will be published in *Cereal Chemistry*.

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No report on baking powders and baking chemicals was given by the referee.

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### DRUG SECTION

#### REPORT ON DRUGS<sup>2</sup>

By ARTHUR E. PAUL (U. S. Food and Drug Administration,  
Chicago, Ill.), *Referee*

Of the 27 subjects studied, only two can be considered closed: Strychnine in tablets and calcium gluconate.

Microchemical methods were recommended for adoption on the following synthetics: Antipyrin, methenamine, and triethanolamine. It is planned to study additional products under this classification. No new subject, other than that of pysillium seed, will be studied, but it is hoped that at the end of the current year it will be possible to complete many of the present subjects.

The Referee, with the assistance of the associate referees and probably of other interested members of the Association, hopes to review all available drug methods and make suitable recommendations for changes and

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<sup>1</sup> For report of Subcommittee C and action of the Association see *This Journal*, 17, 59 (1934).

<sup>2</sup> For report of Subcommittee B and action of the Association, see *This Journal*, 17, 50, 74 (1934).

additions, for use in connection with the next revision of *Methods of Analysis*.

This report should be considered in connection with the reports given by the associate referees. With few minor exceptions, these reports and their recommendations are approved by the Referee. The following comments on each subject constitute a part of this report.

The recommendations for further study of aconite and of psyllium seed are approved.

The Associate Referee on Radioactivity in Foods and Drugs had no opportunity to do the work planned. It is recommended that the subject be continued.

The recommendations of the Associate Referee on Calcium Gluconate, Mercurials, and Microchemical Methods for Alkaloids are approved.

The Associate Referee on Microchemical Methods for Synthetics recommends adoption of methods for antipyrin, methenamine and triethanolamine and further study of amidopyrin, and also suggests additional study on the following subjects: Phenacetin, acetanilid, barbital and its derivations—phenylbarbital, amytal, pentobarbital and dial.

The Associate Referee on Hypophosphites recommended a method to replace directions given in the National Formulary. The National Formulary essentially directs oxidation with nitric acid, evaporation to dryness and then determination of the phosphoric acid formed. The details for this latter determination conform closely to those of the U.S.P. for phosphoric acid and sodium phosphate. The method is volumetric and has been repeatedly shown to be inaccurate. W. F. Kunke, U. S. Food and Drug Administration, Chicago, stated:

Theoretically, the procedure appears sound, but practically it is difficult to determine when the neutral point to litmus has been reached. Presumably any free nitric acid would dissolve  $\text{Ag}_3\text{PO}_4$  and excess  $\text{ZnO}$  would occlude  $\text{AgNO}_3$ . Results found by two analysts, 98.2% and 85.2%, confirm the previous experience that the U.S.P. assay is not satisfactory.

In an exhaustive study, entitled "The Assay of Phosphoric Acid," F. A. Maurina (*J. Am. Pharm. Assoc.*, 17, 668) confirms this experience and shows that the method gives erroneous results. He records results obtained by different analysts on the same sample, ranging from 48.5 to 67.1 per cent. He finds that by using zinc hydroxide as a neutralizing medium instead of zinc oxide, highly satisfactory results are obtained.

The Associate Referee developed details involving a gravimetric determination of the phosphoric acid formed by the N.F. assay, and his collaborators reported results quite close to the theoretical figures. His method is quite satisfactory, although it is decidedly longer than the volumetric procedure proposed by Maurina.

It will be necessary next year to continue this subject and to include for study the determination of hypophosphites in mixtures. It is therefore

suggested that a comparative study be made of the two methods, with especial reference to the applicability of each in mixtures, since it seems possible that in each instance the Associate Referee's method may prove more applicable than the volumetric procedure.

No report on *santonin* was submitted. It is suggested that the subject be continued.

The Associate Referee on Ether recommends the tentative adoption of the method for the determination of ether in aqueous and alcoholic solutions which was proposed last year. This recommendation is approved, but it is suggested that there be included under the heading of the method, the phrase, "Not applicable in the presence of essential oils." It is recommended that this subject be continued.

The Associate Referee on Benzyl Compounds reports some promising results, but suggests further study. This recommendation is approved.

The findings of the Associate Referee on Morphine in Sirups show much promise. He recommends that the subject be continued and this recommendation is approved.

The Associate Referee on Guaiacol did no work. It is recommended that the subject be studied next year.

The Associate Referee on Bromide-Bromate Methods suggests that certain changes be made in the present methods involving bromide-bromate titrations. These changes are approved. It is recommended that this topic be discontinued.

The Associate Referee on Rhubarb and Rhaponticum gave a most interesting verbal report illustrated by moving pictures showing the action of cascara on daphnia. Later he submitted a voluminous report on his biological researches involving the reactions of these drugs on the infusorial daphnia. Because of the scope of his work, it was considered that the report should be published elsewhere as a separate article. It therefore has not been included among the associate referees' reports. When it is finally published it will be found to be a most valuable contribution in the field of biological testing.

The Associate Referee on Tetrachlorethylene devised a method for this determination and recommends its adoption. This recommendation is approved. See *This Journal*, 17, 78 (1934).

The Associate Referee on Hexylresorcinol performed no work on this subject. It is recommended that it be reassigned.

The Associate Referee on Ergot Alkaloids devoted much study to this subject and made considerable headway in the development of chemical methods for assaying ergot preparations. He suggests further study and this suggestion is approved.

The Associate Referee on Biological Testing devoted his attention to the subject of ergot and has therefore been unable to submit a further report on the subject of Biological Testing. It is recommended that it be again assigned.

The Associate Referee on Nitrites in Tablets studied several methods. As a result, he recommends collaborative study of the chlorate method. This recommendation is approved.

The Associate Referee on Ointments studied various methods for the examination of iodine ointment, but was not able to carry on a collaborative study. His recommendation for further study is approved, and it is suggested that it include a method for the determination of iodine absorbed by the fat.

The Associate Referee on Acetphenetidin in the Presence of Caffeine and Aspirin devised and studied collaboratively a method for this difficult separation. Because of discordant results submitted, he recommends, and the Referee approves, further study.

The present methods for the determination of strychnine in tablets are applicable to hypodermic tablets, but not to coated tablets or coated triturates. Slight modifications as to details are necessary, and it was expected that the Associate Referee would prepare these directions. He, however, found it impossible to give a report. The Referee therefore submits a method which has been used and found to be adequate. Since these details involve no change in the present methods, but simply aid the analyst in preparing these classes of preparations for analysis, it is recommended that the details be adopted tentatively. The method has been published [*This Journal*, 17, 79 (1934)].

The Associate Referee on Pyridium confined his attention to a survey of the literature and selected several methods for collaborative study. It is recommended that this subject be reassigned to the same Associate Referee.

The Associate Referee on Gums developed some interesting methods for the identification of certain gums. Further study of these is suggested. It is also suggested that a study be made of methods for their identification and separation in mixtures.

The Associate Referee on Essential Oils studied the literature on the subject and recommends that the topic be continued. This is approved.

The Associate Referee on Resins and Oleoresins performed some work on this subject, but his results did not warrant the preparation of a report. It is suggested that this topic be continued.

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## REPORT ON CRUDE DRUGS

By H. W. YOUNGKEN (Massachusetts College of Pharmacy,  
Boston, Mass.), *Associate Referee*

During the past year the problem of aconite has been continued, studies having been made upon the tuberous roots of *Aconitum Napellus* sub-

species *firmum* by the Associate Referee and Collaborators Irwin S. Shupe and James C. Munch.

### MATERIALS AND METHODS

The materials for this investigation consisted of ten authentic plants of *Aconitum Napellus* subspecies *firmum*, several with root systems attached, and about five ounces of roots and stem bases collected by Dr. Zdenek Klan in Czechoslovakia at the request of the Associate Referee. The plants were immediately checked for their identity by comparing with descriptions in Hegi's *Flora von Mittel Europa*, and proved to be authentic. The loose roots were also checked by careful histological comparison with a root system attached to the aerial portion of a plant in the same shipment and found to be authentic.

Specimens of the roots were examined as to physical characteristics and microscopical structure by the Associate Referee and Shupe and for their pharmacodynamic action by Munch. Transverse and radial-longitudinal sections were studied in water, phloroglucin, and hydrochloric acid, and in stained permanent mounts. Scrapings were also examined in water and phloroglucin-hydrochloric acid mounts.

The samples consisted of conical tuberous roots up to 35 mm. in length and up to 15 mm. in width, externally dark brown, longitudinally wrinkled with small rootlets and scars most abundant toward the crown, some pieces showing the parent tuber with one to five small daughter tubers attached. The fracture of the parent tuber was short with a brown horny internal surface, that of the daughter tuber short with a whitish mealy surface. The odor was indistinct and the taste sweetish, soon becoming acrid and developing a tingling sensation which was followed by a sensation of numbness.

#### MICROCHEMIC EXAMINATION (ASSOCIATE REFEREE)

Tests upon alkaloidal material extracted from roots of *A. Napellus* var. *firmum* by the Associate Referee and Shupe gave crystals with sodium carbonate characteristic of aconitine. Small hexagonal plates were obtained.

#### MICROSCOPIC EXAMINATION (ASSOCIATE REFEREE)

##### *Transverse Section*

A. *Lower end*.—Diameter 2 mm.

1. *Epidermis*.—Brown with more or less conical to rounded-conical epidermal cells having suberized outer walls and brown contents.

2. *Primary cortex*.—11 to 12 layers of more or less spherical-shaped starch parenchyma cells. Scattered through this region are many stone cells of various shapes and sizes.

3. *Endodermis*.—Distinct. One layer of tangentially-elongated endodermal cells.

4. *Secondary cortex*.—From 9 to 16 layers of starch parenchyma, the cells being radially arranged. Imbedded in this region are irregular patches of primary sieve tissue arranged in an interrupted circle.

5. *Cambium line*.—Slightly wavy, circular to elliptic, on the inner surface of which are 7 protoxylem strands.

6. *Pith*.—Composed of an intact central zone of starch parenchyma, the cells filled with starch.

B. *Second region*.—Diameter 3 mm.

1. *Epidermis*.—Outer and radial walls of the epidermal cells showed greater suberization than in former region.

2. *Primary cortex*.—Similar to former region but showing slight increase in number of stone cells.

3. *Endodermis*.—A single layer of distinct elongated cells.

4. *Secondary cortex*.—Broader than in former region with 18 rows of cells and showing some secondary sieve bundles cut off from the cambium. A few stone cells had been laid down on the inner face of the endodermis in outer region.

5. *Cambium line*.—More angular than in the former section; 7 angled and showing only slighter deeper xylem strands. Secondary xylem was being laid down as wood parenchyma on the outer face of the protoxylem strands.

6. *Pith*.—Broader and with somewhat larger cells than at lower level.

C. *Third region. Mid zone*.—Diameter 4 mm.

1. *Epidermis*.—Cells more suberized.

2. *Primary cortex*.—Showing an increased number of stone cells.

3. *Endodermis*.—Clear and open looking cells.

4. *Secondary cortex*.—Up to 32 cells broad. It showed an increased number of secondary sieve strands and a few additional stone cells on the inner face of the endodermis.

5. *Cambium line*.—Distinctly 7 angled. In the angles wood parenchyma had been laid down on the inner surface of the cambium which had pushed in the center of each xylem strand.

6. *Pith*.—Broader than in sections at lower levels. Intact.

D. *Fourth level. Between mid-region and summit*.—Diameter 12 mm.

1. *Epidermis*.—Completely suberized and exfoliated at some places.

2. *Primary cortex*.—Partly disintegrated with patches of the outer cell layers suberized. Stone cells abundant and scattered.

3. *Endodermis*.—Considerably modified and indistinct in places.

4. *Secondary cortex*.—Broad zone of starch parenchyma interspersed with patches of sieve tissue and with a few stone cells near endodermis.

5. *Cambium line*.—Irregular, elliptical, almost indistinct in places with xylem bundles tending to be spread out along portions of line. Many tracheae coursing in oblique to longitudinal directions.

6. *Pith*.—Starch parenchyma showing partial disintegration.

E. *Fifth Region. Just below summit*.—Diameter 14 mm.

1. *Metaderm*.—Representing suberized primary cortex, endodermis, and a portion of the outer region of the secondary cortex.

2. *Secondary cortex*.—Of starch parenchyma traversed in places by xylem bundles.

3. *Cambium line*.—Broken and indistinct, the vestiges of same exhibiting longitudinally to obliquely emanating xylem bundles which extend through parts of secondary cortex.

4. *Pith*.—Large central zone of starch parenchyma.

*Longitudinal Section*

A radial longitudinal section through the thick upper region showed the following structures: Reticulate and pitted tracheae and tracheids predominate; pitted trachea with slit-like pores; the tracheae showing oblique and horizontal end walls; scalariform tracheae few.

*Scrapings*

Scrapings showed the starch grains to be single, spheroidal and 2- to 5-compound, the individual grains measuring from 5 to 20 microns in diameter. Stone cells, reticulate, scalariform and pitted tracheae and tracheids also were found.

## MACROSCOPIC EXAMINATION (I. S. SHUPE)

Sample consisted of two parent tubers, one of which was unsound with pith and central portion dark brown. The other tuber measured 35 mm. in length and 15 mm. maximum width; externally dark brown and longitudinally wrinkled with small rootlets and scars near the crown; fracture showed light brown mealy surface.

## MICROSCOPIC EXAMINATION (I. S. SHUPE)

Scrapings showed single and up to 4-compound starch grains, single grains measuring from 5 microns to 20 microns in diameter. Stone cells, pitted tracheae, and starch-parenchyma cells were observed.

*Transverse sections*

A. *Lower end*.—Diameter 4 mm.

1. *Epidermis*.—With suberized walls.
2. *Primary cortex*.—About 10 layers of starch containing parenchyma cells. Many stone cells of various sizes and shapes.
3. *Endodermis*.—Distinct. One layer of elongated cells.
4. *Secondary Cortex*.—About 40 cells of starch-containing parenchyma with a few stone cells near endodermis and interspersed with patches of sieve tissue.
5. *Cambium line*.—Circular with seven open collateral groups of bundles containing a few brown colored tracheae.
6. *Pith*.—Intact, composed of starch containing parenchyma cells.

B. *Mid region*.—Diameter 9 mm.

1. *Primary cortex*.—Thin and partly disintegrated with many stone cells in small area.
2. *Endodermis*.—Indistinct and separated in places from the primary cortex.
3. *Secondary cortex*.—Intact.
4. *Cambium line*.—Irregular circular with seven V-shaped groups of fibrovascular bundles.
5. *Pith*.—Partly disintegrated.

C. *Near summit*.—Diameter 12 mm.

1. *Epidermis*.—Suberized cells of the remaining portion of the primary cortex and in places the suberized outer cells of the secondary cortex.
2. *Cambium line*.—Indistinct.
3. *Secondary cortex*.—Irregular and deep groups of xylem bundles.
4. *Pith*.—Large, intact, with no symmetry.

D. *Radial longitudinal sections*.

1. *Epidermis*.—Suberized.

2. *Primary cortex*.—Stone cells and starch parenchyma.
3. *Endodermis*.—1 layer slightly elongated cells.
4. *Secondary cortex*.—Square starch parenchyma cells.
5. *Cambium line*.—Pitted tracheae and parenchyma in xylem.
6. *Pith*.—Elongated starch-parenchyma cells.

Transverse sections through the unsound tuber near the lower end showed practically the same characteristics as the sound tuber with the exception of darker color and disintegration in places. The circular cambium line had seven groups of bundles composed of pitted tracheae.

The test for aconitine made by tasting produced a tingling, followed by numbing sensation. See Microchemic examination.

A second sample consisting of parent tubers showed a brownish gray fractured surface and internally the xylem strands showed only a small amount of brown color. They were not filled with brown, resinous material as were the other tubers.

#### PHARMACODYNAMIC TEST

Munch reported to the Associate Referee on one pharmacodynamic test carried out upon roots of this species. He found this material nearly seven times more powerful than U.S.P. aconite.

As there are roots of other subspecies of *Aconitum* still to be obtained and worked upon, it is recommended<sup>1</sup> that the subject of aconitum be continued. It is also recommended that the subject of psyllium seeds be taken up during the coming year.

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No report on radioactivity in foods and drugs was given by the associate referee.

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#### REPORT ON CALCIUM GLUCONATE

By HARRY J. FISHER (Agricultural Experiment Station,  
New Haven, Conn.), *Associate Referee*

Since last year's report<sup>2</sup> was submitted the attention of the Associate Referee has been called to a method for the determination of calcium gluconate proposed by de Carli.<sup>3</sup> This method depends on the measurement of the rotation of solutions of calcium gluconate containing bismuth nitrate. As the enhancement in rotation produced by bismuth according to de Carli's figures was much less than that observed with uranium by the Associate Referee's method it seemed unnecessary to study this method.

The somewhat unsatisfactory results of the collaborators on last year's samples led to a more exhaustive study this year of the details of the uranium acetate method. A supply of pure calcium gluconate was prepared by recrystallizing Eastman calcium gluconate from water, washing

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<sup>1</sup> For report of Subcommittee B and action of the Association, see *This Journal*, 17, 50 (1934).

<sup>2</sup> *This Journal*, 16, 379 (1933).

<sup>3</sup> *Ann. chim. applicata*, 21, 465 (1931); Gualdoni, *Boll. chim.-farm.*, 71, 45 (1932).



with alcohol and ether, and drying overnight at 70° in vacuo and then for several weeks in a desiccator. The average of several determinations of the calcium content of the purified salt by evaporation with sulfuric acid followed by ignition showed it to be 99.97 per cent pure anhydrous calcium gluconate.

Although it is possible to read calcium gluconate solutions in a saccharimeter using white light, and all previous work had been done in this manner, it was felt that the use of a light filter might lead to greater uniformity in results between collaborators using different instruments. Therefore in all observations made this year a 50 mm. tube containing a solution of 1.8 grams of potassium dichromate in 100 cc. was placed in the saccharimeter.

#### TEMPERATURE VARIATIONS

A solution of calcium gluconate containing 2 grams per 100 cc. at 20°C. when polarized at 20° showed a rotation of +1.3°V. The same solution cooled to 15° had an identical rotation; when warmed to 25° the rotation was +1.2°V. The effect of small temperature differences on the rotation of pure calcium gluconate solutions can therefore be considered negligible.

#### VARIATION IN QUANTITY OF URANYL ACETATE USED

As it is obviously not desirable to use a larger quantity of uranyl acetate than is necessary to insure saturation, since the undissolved material reduces the actual volume of solution in the flasks, experiments were conducted to determine whether the quantity of uranium acetate could be reduced below the 20 grams per 100 cc. used previously. It was found that 14 grams of uranyl acetate per 100 cc. was sufficient to produce a maximum rotation with a minimum of undissolved salt.

#### CLARIFICATION OF SOLUTIONS

Samples containing cocoa require the use of some clarifying agent to produce solutions that are clear enough to be read in a saccharimeter. In this work alumina cream was used. Even with this material, however, the solutions that had been saturated with uranyl acetate were quite dark, and some collaborators found it impossible to read them in a 200 mm. tube. An attempt was made to find a more efficient clarifying agent. It was found that 1 cc. of bromine water sometimes gave slightly better clarification than did the alumina cream, but not uniformly so. On the whole alumina cream seemed the most satisfactory.

#### INFLUENCE OF ACIDITY AND ALKALINITY ON ROTATION

It is known that any marked acidity or alkalinity will affect the rotation of these complexes of active hydroxy acids with heavy metals. Dunbar and Bacon<sup>1</sup> originally substituted uranyl acetate for uranyl nitrate in

<sup>1</sup> *J. Ind. Eng. Chem.*, 3, 826 (1911).

the determination of malic acid because of the lower hydrogen-ion concentration of solutions of this salt. Lutz and Jirgensons<sup>1</sup> found the rotation of solutions of sodium gluconate containing sodium molybdate to be highly dependent upon the acidity or alkalinity of the solutions. The Associate Referee undertook a number of experiments to determine the magnitude of this effect in the case of solutions of calcium gluconate saturated with uranyl acetate.

An actual determination of the *pH* of a solution saturated with uranyl acetate is difficult. Colorimetric *pH* determinations are impossible, and determinations using the quinhydrone electrode in the presence of the reducible uranyl ion must be regarded with suspicion.<sup>2</sup> Therefore, while the change in rotation is presumably a function of the hydrogen-ion concentration, in the chart the rotations of the solutions were plotted against moles of acid or base per mole of calcium gluconate.

The procedure used was as follows:

A quantity of calcium gluconate that would yield a 0.05 molar solution was weighed into a 25 cc. volumetric flask, and the amount of standard normal hydrochloric acid or sodium hydroxide added that corresponded to a definite number of moles of acid or base per mole of calcium gluconate. Sufficient water was added to bring the total volume to 15 cc.; the solution was warmed until the calcium gluconate dissolved and cooled; 3.5 grams of uranyl acetate was added; and the flask was shaken for 1 hour. The contents of the flask were then made to volume at 20°C. with saturated uranyl acetate, filtered, and polarized at 20°. The results are shown in Fig. 1. The curve could not be carried beyond 6 moles of sodium hydroxide per mole of calcium gluconate because greater alkalinity caused precipitation of sodium uranate.

The curve shows that the rotation increases progressively with increasing alkalinity up to between 3.5 and 4 moles of base per mole of calcium gluconate; further addition of alkali causes no change in rotation. The significance of this in the use of the method for the determination of calcium gluconate is not so much that the maximum rotation is only obtained in alkaline solutions as that only when the solution has an alkalinity corresponding to more than 4 moles of base per mole of calcium gluconate is the rotation unaffected by slight changes in the *pH*.

When this fact was discovered, an attempt was made to modify the method for the determination of calcium gluconate in the presence of cocoa by the addition of alkali to the solutions to be polarized. No satisfactory means of clarifying such solutions could be found, however. Although the addition of lead acetate to alkaline solutions containing calcium gluconate and cocoa produced filtrates that were clear and nearly

<sup>1</sup> *Ber.*, 65 B, 784 (1932).

<sup>2</sup> Two per cent solutions of calcium gluconate in water and saturated uranyl acetate showed apparent *pH* values by the quinhydrone method of 6.68 and 3.54, respectively.

colorless at first, these solutions quickly clouded, and the addition of lead to the solutions seemed unsafe in view of the fact that May, Weisberg and Herrick had shown<sup>1</sup> that lead gluconate is laevo-rotatory.

#### COLLABORATIVE WORK

Two samples were submitted to collaborators for study. Sample 1 was the purified calcium gluconate previously described. Sample 2 was a mixture of one-half calcium gluconate, one-fourth cocoa, and one-eighth each calcium lactate and lactose. It contained 49.99 per cent of anhydrous calcium gluconate.

The collaborators were requested to standardize their saccharimeters with a solution of Bureau of Standards sucrose and on the basis of this standardization to make such corrections as were necessary in their reported readings on the samples.

Both Samples 1 and 2 were requested to be analyzed by the method as published,<sup>2</sup> using 0.5 gram portions of Sample 1 without alumina cream and 1 gram portions of Sample 2 with alumina cream. The actual observed rotations were asked for, not calculations of the amount of calcium gluconate in the samples. To study the effect of the time of shaking, collaborators were requested to report results obtained with the uranyl acetate-saturated solutions after shaking 1, 2 and 3 hours. Sample 1 was also directed to be analyzed by dissolving the 0.5 gram in each flask in a mixture of 5 cc. of normal NaOH and 10 cc. of water, instead of 15 cc. of water, and proceeding from then on in the same manner as before. Readings of the uranyl acetate-saturated solutions of Sample 2 were requested both in 100 mm. and 200 mm. tubes if possible.

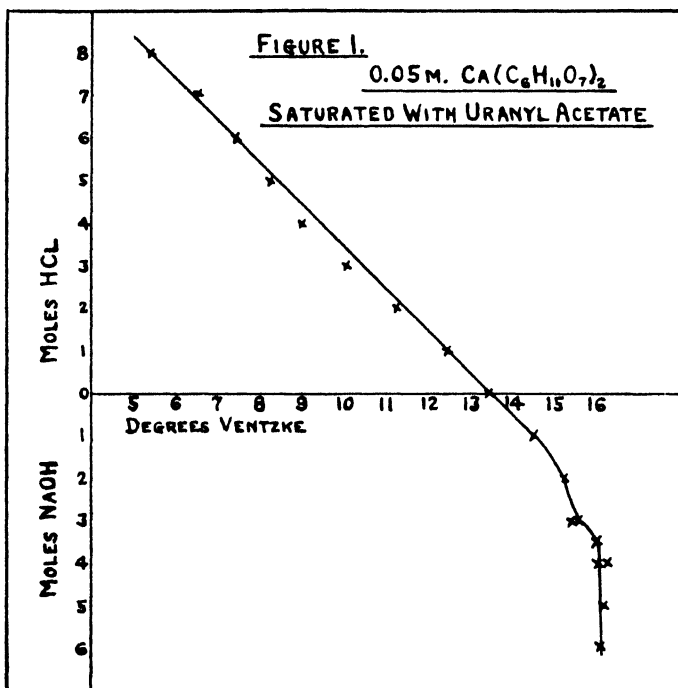
All the results obtained by the seven collaborators (Tables 1 and 2) were corrected for errors in calibration of the saccharimeters. The differences between rotations with and without uranyl acetate listed in Table 1 are calculated on the basis of one hour's shaking with uranyl acetate. In working with Sample 2, Haring, Tucker and Marsh and Reindollar shook their solutions for 3 hours and Shupe for 1½ hours; all other collaborators used a shaking period of 1 hour.

The Associate Referee considers that these results agree as closely as could be expected when many different collaborators are using different instruments, particularly when the difficulty of reading the average saccharimeter to even 0.1° Ventzke is considered. It should be particularly noted that the value for the factor  $F$  in the formula  $X = F(B - A)$  ( $X$  = per cent calcium gluconate,  $B$  = rotation of solution saturated with uranyl acetate,  $A$  = rotation of solution without uranyl acetate), obtained from the average difference in rotation given in Table 2, is 4.34, while half the value similarly obtained from the results of Table 1 (no sodium hydroxide)

<sup>1</sup> *J. Washington Acad. Sci.*, 19, 445 (1929).

<sup>2</sup> *This Journal*, 17, 75 (1934).

is 4.26. This shows good agreement in results on pure calcium gluconate and on preparations containing in addition cocoa, sugar and calcium lactate, in contrast to the results of last year, when agreement on the sample containing calcium lactate was very poor, and when the factor obtained in the presence of cocoa differed from that obtained on the pure salt. The factor 4.26 for anhydrous calcium gluconate corresponds to 4.44 for the monohydrate, as against the average factor 4.42 found on Sample 2 of last year.



Although the data on the effect of acids and alkalis obtained by the Associate Referee (summarized in Fig. 1) point toward a theoretical advantage in the use of excess alkali with the uranyl acetate, since the preparations which are on the market are all neutral and since the alkali method cannot be used except with the pure salt, it is not considered that the practical advantages of the alkali method are such as to make advisable the adoption of a different method for the pure salt than that for mixtures. The observations of the collaborators on the time of shaking the solutions show that with proper agitation one hour's shaking is sufficient. It is believed that the use of a light filter is advantageous, and that the method should be rewritten to allow when necessary the use of a 100 mm. tube in reading solutions. It has also been thought advisable to

TABLE 1.—*Calcium gluconate, Ca(C<sub>6</sub>H<sub>11</sub>O<sub>7</sub>)<sub>2</sub>, 99.97 per cent.*

COLLABORATORS	OBSERVED ROTATION, 200 MM. TUBE													
	WITHOUT SODIUM HYDROXIDE					WITH SODIUM HYDROXIDE								
	WITHOUT URANYL ACETATE	WITH URANYL ACETATE			DIFFER- ENCE	WITHOUT URANYL ACETATE	WITH URANYL ACETATE			DIFFER- ENCE				
		TIME OF SHAKING					TIME OF SHAKING							
		1 HR.	2 HR.	3 HR.			1 HR.	2 HR.	3 HR.					
°V.	°V.	°V.	°V.	°V.	°V.	°V.	°V.	°V.	°V.					
S. W. Bower, Direct Sales Co., Inc., Buf- falo, N.Y.	1.0	12.75			11.75	1.1	14.75			13.65				
H. J. Fisher	1.22	12.95	12.83	12.80	11.73	1.49	15.39	14.93	14.97	13.90				
M. M. Haring, University of Maryland, College Park, Md.	0.96	12.05	13.22	13.54	11.09	1.08	15.28	14.67	14.21	14.20				
C. S. Leonard, The Burroughs Wellcome Co., Tuckahoe, N.Y.	1.09	13.05	13.10	13.06	11.94	1.18	14.79			13.61				
E. K. Tucker and G. H. Marsh, Dept. of Agriculture and Industries, Montgomery, Ala.	1.05	12.21	12.35	12.50	11.16	1.23	14.75	14.85	14.67	13.52				
W. F. Reindollar, State Dept. of Health, Baltimore, Md.	1.24	12.88	12.81	13.01	11.64	1.17	15.03	15.20	15.32	13.86				
I. S. Shupe, U.S. Food and Drug Adm., Chicago, Ill.	1.5	13.6	13.6	13.6	12.1	1.6	14.8			13.2				
L. Longfield-Smith, State Agricultural Dept., Tallahassee, Fla.	0.8	13.2	13.0	13.0	12.4	1.1	15.4	15.2	15.2	14.3				
Average					11.73					13.78				

change the factor for calculation so that results are obtained in terms of anhydrous calcium gluconate, as the work of May, Weisberg and Herrick indicates that this is the stable form of the salt.

### RECOMMENDATIONS<sup>1</sup>

It is recommended that the method for the determination of calcium gluconate previously published<sup>2</sup> be adopted as official, first action, with the following changes:

(1) Insert the phrase "Applicable to preparations whose aqueous solutions are neutral and which do not contain salts of other optically active hydroxy acids" above the directions for the method.

(2) Change "20 cc." in the third sentence to "15 cc."

(3) Change the fourth sentence to read, "Cool to room temperature, to one flask add 3.5 grams of pulverized uranyl acetate, stopper, and place the mixture in a shaking machine for 1 hour (if agitation is not sufficiently vigorous, more than one hour's shaking may be required)."

(4) Change the next to last sentence to read, "Filter, and polarize each solution in a 200 mm. tube, using a 50 mm. tube containing a 1.8 per cent solution of  $K_2Cr_2O_7$  as a light filter. If a solution is too dark to read in a 200 mm. tube, make the reading in a 100 mm. tube and multiply the result by 2."

(5) Change the last sentence to read "If A equals the rotation in degrees Ventzke of the solution containing no uranyl acetate, and B the rotation of the solution saturated with uranyl acetate, with 1 gram samples the percentage of  $Ca(C_6H_{11}O_7)_2 = 4.34 (B - A)$ , and with 0.5 gram samples the percentage of  $Ca(C_6H_{11}O_7)_2 = 8.52 (B - A)$ ."

TABLE 2.—*Calcium gluconate mixture—49.99 per cent  $Ca(C_6H_{11}O_7)_2$ .*

COLLABORATORS	OBSERVED ROTATION					
	WITHOUT URANYL ACETATE		WITH URANYL ACETATE		DIFFERENCE	
	100 MM TUBE	200 MM TUBE	100 MM TUBE	200 MM TUBE	200 MM TUBE	TWICE 100 MM TUBE READING WITH URANYL ACETATE—200 MM TUBE READING WITHOUT URANYL ACETATE
	°V.	°V.	°V.	°V.	°V.	°V.
Fisher		2.91	7.36	14.26	11.35	11.81
Haring	1.20	2.25	6.98	14.61	12.36	11.71
Leonard	1.36	2.68	6.89	13.84	11.16	11.10
Tucker and Marsh	1.25	2.46	6.80	13.50	11.14	11.14
Reindollar	1.48	2.23	6.99			11.75
Shupe		2.8	7.0			11.2
Longfield-Smith		2.6	7.3			12.0
Average					11.50	11.53

<sup>1</sup> For report of Subcommittee B and action of the Association, see *This Journal*, 17, 51, 75 (1934).

<sup>2</sup> *This Journal*, 15, 465 (1932).

## REPORT ON MERCURIALS

By ERNEST C. DEAL (Food and Drug Administration,  
New Orleans, La.), *Associate Referee*

This subject has been considered each year since 1924. Many methods have been tried out on various products with different degrees of success. With the appearance of the U.S.P.X., assays were given for a number of products containing mercury in various forms. Other assays were worked out by the associate referees applicable to products for which no specific assay was given in the U.S.P. or N.F.

No collaborative work was reported last year, and Subcommittee B recommended that the subject be continued to include mercury-containing dyes represented as antiseptics.

Accordingly, the Associate Referee undertook to give consideration to this class of compounds. Owing to the wide use of mercurochrome it was employed in this year's work as a type.

A description of mercurochrome-220 soluble is given in the literature<sup>1</sup> together with an assay. Other methods have been published<sup>2</sup> for the analysis of this product. So far as noted, all limit the assay to a determination of total mercury. Mercurochrome almost invariably reaches the consumer as a water solution containing approximately 2 per cent of the dye. Consequently it was thought desirable to work out a method directly applicable to the analysis of these solutions.

Four methods for the destruction of organic matter were tried out by the Associate Referee, viz.:

- (1) Wet combustion with sulfuric and nitric acids.
- (2) Free chlorine from hydrochloric acid and potassium chlorate.
- (3) Alkaline oxidation with potassium permanganate.
- (4) Oxidation with potassium permanganate in the presence of sulfuric acid.

Of the methods tried out, No. 4 was most satisfactory from the standpoint of accuracy and ease of operation. Mercury was finally determined by both the sulfide method and the Rupp formaldehyde method. The thiocyanate method was found to be inapplicable owing to the presence of bromine in the compound. For some unaccountable reason consistently high results were obtained by the Rupp method. Consequently it was decided to use the sulfide method exclusively. A solution of Mercurochrome was prepared and sent out to the collaborators with instructions to determine total mercury and total solids according to the procedures outlined. These methods have been published [*This Journal*, 17, 75 (1934).]

The collaborators' results are shown in the table.

From the results obtained by the collaborators it is believed that the method of assay is satisfactory. The Associate Referee further believes

<sup>1</sup> New and non-official remedies, 1923, p. 191.

<sup>2</sup> *Quart. J. Pharm., Pharmacol.*, June 10, 1931.

COLLABORATOR	SOLIDS	MERCURY	
	grams per 100 cc. solution	grams per 100 cc. solution	per cent in solids
Harry S. Haller	1.908	0.487	25.52
New Orleans	1.909	0.487	25.51
Andrew M. Allison	1.935	0.498	25.75
New York City	1.911	0.493	25.81
	1.931		
M. J. Gnagy	1.909	0.479	25.09
New Orleans	1.908	0.479	25.10
Irwin S. Shupe	1.88	0.480	25.5
Chicago	1.88	0.484	25.7
John C. Krantz, Jr.	2.044	0.491	24.02
Baltimore	2.051	0.475	23.16
Sylvan B. Falck	1.916		
New Orleans	1.911	0.472	24.70
E. C. Deal	1.908	0.476	24.95
	1.915	0.480	25.06
	1.913	0.477	24.93

that any likely sophistication would be detected by the proposed tests. Since mercurochrome-220 soluble contains varying amounts of moisture up to 10 per cent, an arbitrary figure should be accepted and an arbitrary procedure adopted for its determination. It is believed that the proposed methods will furnish the information desired for determining the strength and purity of the popular solutions sold.

It is accordingly recommended<sup>1</sup> that the methods presented for the determination of total mercury and total solids and the proposed tests for determining purity be adopted as tentative.

## REPORT ON MICROCHEMICAL METHODS FOR ALKALOIDS

By C. K. GLYCART (U. S. Food and Drug Administration,  
Chicago, Ill.), *Associate Referee*

In accordance with the recommendation made last year, study of methods of identification for hyoscyne, hyoscyamine, homatropine, and papaverine was continued. In the preliminary work hyoscyne responded readily to the test reagents, but homatropine and particularly hyoscyamine yielded no tests with Wagner's reagent, the official test reagent for atropine, sufficiently characteristic to distinguish the crystals from atropine. Because no time was available to complete the work this year, these atropine alkaloids will be studied as a group next year.

<sup>1</sup> For report of Subcommittee B and action of the Association, see *This Journal*, 17, 51, 75 (1934).



Papaverine produced definite crystals with zinc chloride reagent. Procaine hydrochloride, although not an alkaloid, was included since its general properties are similar to cocaine. The directions for the tests and control specimens, consisting of papaverine hydrochloride and procaine hydrochloride, also samples labeled No. 1 and No. 2, for identification, were sent to the collaborators. Sample 1 consisted of compressed tablets containing procaine hydrochloride; Sample 2 contained a solution of 1:100 papaverine hydrochloride.

The method has been published [*This Journal*, 17, 76 (1934)].

The results and comments follow:

*H. McCausland, Abbott Laboratories, North Chicago, Ill.*—Papaverine and zinc chloride.—Thin rectangular plates. Procaine and platinic chloride.—Spherical crystals, singly and in clusters, rather slow in forming. The unknown samples were identified as: No. 1—Procaine and No. 2—Papaverine.

*C. C. Fulton, Bureau of Industrial Alcohol, Minneapolis, Minn.*—No. 1 (tablet) was identified as procaine. Dark rosettes or spherocrystals, macroscopically orange. Better identification test by gold chloride and HCl. No. 2 (solution) was identified as papaverine. Zinc chloride forms colorless square plates. The sensitivity is increased by a rather high concentration of HCl in the test drop.

*F. C. Sinton, U. S. Food and Drug Administration, New York.*—No. 1—Procaine, and No. 2—Papaverine.

No difficulty was encountered in recognizing the unknowns by comparison with the control and description.

In the case of the papaverine the crystals seemed to be generally rectangular. However, an additional feature of the crystals was observed, namely, the cut in corners which appeared to be quite characteristic.

The spherical crystals described under procaine were observed, but these appeared after some standing. At first large numbers of crystals in the form of plates appeared, rather irregular in shape but mostly with wedges cut into both ends.

*E. O. Eaton, U. S. Food and Drug Administration, San Francisco.*—No. 1—Procaine, No. 2—Papaverine.—By comparing the microcrystals formed by reagents with knowns. However, in absence of knowns I doubt if your word-picture of crystals formed would be entirely adequate.

## DISCUSSION

The results of the collaborators show that the tests for papaverine and procaine are satisfactory. Fulton states that gold chloride and hydrochloric acid also make a satisfactory test for procaine. This was confirmed by the Associate Referee, and the test was added to the method.

## RECOMMENDATIONS<sup>1</sup>

It is recommended—

(1) That the microchemical tests presented for papaverine and procaine be adopted as tentative methods.

(2) That further study be made on tests for the identification of hyosine, hyoscyamine, homatropine, and atropine.

<sup>1</sup> For report of Subcommittee B and action of the Association, see *This Journal*, 17, 51 (1934).

## REPORT ON MICROCHEMICAL METHODS FOR SYNTHETICS

By IRWIN S. SHUPE (U. S. Food and Drug Administration,  
Chicago, Ill.), *Associate Referee*

In 1932, benzocaine, cinchophen, chinisol and pyridium were studied. This year antipyrine, amidopyrine, methenamine, and triethanolamine were studied collaboratively.

According to Wilson,<sup>1</sup> triethanolamine,  $N(C_2H_4OH)_3$ , a new commercial material, is a non-corrosive organic base related to ammonia. It is a clear, colorless viscous material with specific gravity of 1.12 at 20°C., and boiling point 277°C. at 150 mm. pressure. It is entirely soluble in water and alcohol, and it is not extractable from water solutions with immiscible solvents.

The commercial product, containing approximately 17.5 per cent diethanolamine and 5 per cent monoethanolamine, is used in the preparation of many cosmetics, such as washable cold creams, rouges, grease paints, cleansing creams, and soaps. It is also used as an emulsifying agent in the preparation of "soluble oils," polishes, cleaning compounds, and tree-spraying materials.

The amidopyrine, antipyrine, and methenamine used for the tests were products of reputable manufacturers and complied with U.S.P. requirements.

In preliminary tests the reagents given in the table were found to produce one or more crystalline precipitates with 1 per cent of the synthetics in water solution.

Crystalline precipitates are indicated by (c); non-crystalline by (a); and no reaction by (-).

REAGENTS	AMIDOPYRINE	ANTIPIRINE	METHENAMINE	TRIETHANOLAMINE
Wagner's†	c	c	c	—
Gold chloride*	c	a	c	a
Marme's†	c	a	c	a
Kraut's†	c	a	c	c
Silico-tungstic acid	a	a	c	—
Bromine water (Sat. Soln.)	a	a	c	—
Picric acid (Sat. water Soln.)	c	c	c	—
Potassium Ferrocyanide*	—	c	—	—
Mercuric chloride*	c	a	c	a

\* Consists of approximately 5 per cent solution in water.

† *Methods of Analysis*, A.O.A.C., 1930.

For amidopyrine, mercuric chloride was considered to be the most characteristic reagent. In dilutions up to 1:1000, clusters of curving needles and a few rectangular plates are formed.

<sup>1</sup> *Ind. Eng. Chem.*, 22, 143 (1930).

Antipyrine<sup>1</sup> is readily distinguished by the formation of crystalline precipitate with acidified potassium ferrocyanide. The test is sensitive to about 1:300 concentration of antipyrine.

Methenamine is one of a few compounds that produce a crystalline precipitate with silicotungstic acid reagent. The crystals are very thin and can best be seen in dilute solutions. A 1:10,000 solution of methenamine will yield small rectangular plates best seen in reflected light.

Triethanolamine with Kraut's reagent forms globules changing into large orange-colored plates. In a 1:1000 solution small crystals are formed immediately.

Directions for tests, control specimens, and unknown samples for identification were sent to collaborators. The unknown samples consisted of water solutions of the synthetics in 1:100 concentration. No. 1 contained antipyrine; No. 2, amidopyrine; No. 3, methenamine, and No. 4, triethanolamine.

The method has been published [*This Journal*, 17, 77 (1934)].

#### RESULTS OF COLLABORATORS

*E. O. Eaton, Food and Drug Adm., San Francisco.*—I. Antipyrine; II. Amidopyrine; III. Methenamine; and IV. Triethanolamine. The tests of amidopyrine and methenamine do not appear to be very characteristic.

*H. McCausland, Abbott Laboratories, North Chicago, Ill.*—I. Antipyrine; II. Amidopyrine; III. Methenamine; and IV. Triethanolamine. Numbers I and IV seem to give the most striking crystal forms. I find Kraut's reagent unreliable, unless freshly prepared.

*Wm. J. McCarthy, Food and Drug Adm., Cincinnati.*—I. Antipyrine; II. Amidopyrine; III. Methenamine; and IV. Triethanolamine.

One sample (II) with  $\text{HgCl}_2$ .—Crystals in two planes, lower plane adhering to glass, needle shape, curving, fernlike crystals. Top plane, small pyramid-shaped crystals with square base in chain formation and some clusters.

One sample (III) with silicotungstic acid.—Thin rectangular transparent plates.

*Henry R. Bond, Food and Drug Adm., Chicago.*—

	Reagent	Remarks
I. Antipyrine	$\text{K}_4\text{Fe}(\text{CN})_6$	Prismatic crystals, an addition of one drop of 10% $\text{HCl}$ .
II. Amidopyrine	$\text{HgCl}_2$	Prismatic rods principally in clusters.
III. Methenamine	Silicotungstic Acid	Thin transparent rectangular crystals.
IV. Triethanolamine	Kraut's Reagent	Oily globules crystallizing into large red plates and smaller prisms.

*J. H. Cannon, Food and Drug Adm., Chicago.*—I. Antipyrine; II. Amidopyrine; III. Methenamine; and IV. Triethanolamine.

*George M. Johnson, Food and Drug Adm., Chicago.*—I. Antipyrine; II. Amidopyrine; III. Methenamine; and IV. Triethanolamine. Methenamine and amidopyrine give very similar crystals with mercuric chloride and might cause confusion.

<sup>1</sup> Beilstein, *Handbuch der organischen Chemie*, 3rd ed., Vol. IV, p. 510.

Frank C. Sinton, *Food and Drug Adm., New York*.—I. Antipyrine; II. Amidopyrine; III. Hexamethylamine; and IV. Triethanolamine.

The crystal formations in each case were very characteristic and quite easily identified from the descriptions and comparison with the controls.

#### DISCUSSION

The unknown samples were correctly identified by each of the seven collaborators. The tests for antipyrine, methenamine, and triethanolamine are considered satisfactory. The use of mercuric chloride as a reagent for amidopyrine has caused confusion because of a somewhat similar crystalline precipitate formed with methenamine. In an actual analysis the two compounds would probably never be confused because amidopyrine is extracted from alkaline solutions by immiscible solvents, whereas methenamine is not extractable from aqueous solutions. Owing to this difference in properties of the compounds, the test was considered satisfactory for practical purposes. However, it is considered desirable to do more work on the test for amidopyrine since two collaborators report the test not characteristic.

The microchemical test for triethanolamine with Kraut's reagent was devised during regulatory analysis of a drug sample containing this product. The test is designed for the commercial product and is applicable in the presence of glycerine.

#### RECOMMENDATIONS<sup>1</sup>

It is recommended—

(1) That the microchemical methods submitted for antipyrine, methenamine and triethanolamine be adopted as tentative.

(2) That further study be made of amidopyrine and other important synthetics.

#### REPORT ON HYPOPHOSPHITES

By HENRY R. BOND (U. S. Food and Drug Administration,  
Chicago, Ill.), *Associate Referee*

No collaborative work has been reported on methods of analysis for hypophosphites since the subject was first given consideration by the Association in 1931.

Four hypophosphites having essentially the same assay method, those of calcium, manganese, potassium and sodium, are recognized in National Formulary V. The assay prescribes oxidation to the phosphate with nitric acid, followed by a volumetric determination with standard silver nitrate solution. In the analysis of samples in regulatory work, experience has shown the assay to be productive of inconsistent results. The same volu-

<sup>1</sup> For report of Subcommittee B and action of the Association, see *This Journal*, 17, 51, 77 (1934).

metric method is required by U.S.P. X. in the assay of sodium phosphate.

Available literature on the subject of hypophosphites involves two types of determinations:<sup>1</sup> (1) Oxidation to a phosphate with subsequent precipitation of the phosphate; and (2) reduction by the hypophosphite of mercuric chloride to mercurous chloride. Determinations were attempted with each type, with results that appear to be satisfactory with the first method, and with findings by use of the second type of reaction that are as yet unsatisfactory, but which show promise.

A sample of sirup of calcium hypophosphite, prepared according to N. F. V. formula, was sent out for collaborative work. The method employed was supplemented by a method for the determination of calcium, the results to be used as a check on the amount of calcium hypophosphite in the sample. The calcium hypophosphite used in preparation of the sample assayed 99.42 per cent by phosphate precipitation and 100.23 per cent by precipitation of calcium. The hypophosphorous acid, sp. gr. 1.125 at 25°C., assayed 30.8 per cent  $\text{H}_3\text{PO}_2$  by U. S. P. assay. Method and results follow:

#### GRAVIMETRIC DETERMINATION OF HYPOPHOSPHITE

##### REAGENTS

(Applicable in absence of phosphates; if phosphates are present, make suitable corrections.)

(a) *Molybdate solution*.—Dissolve 100 grams of molybdic acid ( $\text{MoO}_3$ ) in a mixture of 144 cc. of  $\text{NH}_4\text{OH}$  and 271 cc. of  $\text{H}_2\text{O}$ . Pour this solution slowly and with constant stirring into a mixture of 489 cc. of  $\text{HNO}_3$  and 1148 cc. of  $\text{H}_2\text{O}$ . Keep the final mixture in a warm place for several days or until a portion heated to 40° deposits no yellow precipitate of  $\text{NH}_4$ -phosphomolybdate. Decant the solution from any sediment and preserve in a glass-stoppered vessel.

(b) *Ammonium nitrate solution*.—Dissolve 100 grams of commercial  $\text{NH}_4\text{NO}_3$ , phosphate-free, in  $\text{H}_2\text{O}$  and dilute to 1 liter.

(c) *Magnesia mixture*.—Dissolve 11 grams of  $\text{MgO}$  in  $\text{HCl}$  (1+4), avoiding an excess of the acid; add a little  $\text{MgO}$  in excess; boil a few minutes to precipitate  $\text{Fe Al}$ , and  $\text{P}_2\text{O}_5$ ; filter. To filtrate add 140 grams of  $\text{NH}_4\text{Cl}$  and 130.5 cc. of  $\text{NH}_4\text{OH}$  and dilute to 1 liter.

(d) *Ammonium hydroxide for washing*.—Dilute 100 cc. of  $\text{NH}_4\text{OH}$  to 1 liter. (This solution should contain not less than 2.5% of  $\text{NH}_3$  by weight.)

##### DETERMINATION

Measure sample to the mark in a 25 cc. volumetric flask. Rinse contents into a 100 cc. volumetric flask, dilute to mark, and mix thoroughly. Pipet a 10 cc. aliquot into a 200 cc. Erlenmeyer flask. Add 25 cc. of  $\text{HNO}_3$  and boil until volume is reduced to 2–3 cc.; add 10 cc. of  $\text{HNO}_3$  and boil until volume is again reduced to 2–3 cc. Cool, and add 20 cc. of water. Add  $\text{NH}_4\text{OH}$  in slight excess and barely dissolve the precipitate formed with a few drops of  $\text{HNO}_3$ , stirring vigorously. To the hot solution add 70 cc. of the molybdate solution for every decigram of  $\text{P}_2\text{O}_5$  present. Digest at about 65° for 1 hour, and determine whether or not the  $\text{P}_2\text{O}_5$  has been completely precipitated by the addition of more molybdate to the clear supernatant liquid. Filter, and wash with cold water, or preferably with the  $\text{NH}_4\text{NO}_3$  solution.

<sup>1</sup> Treadwell and Hall, Vol. 2, pp. 327–8.

Dissolve the precipitate on the filter with  $\text{NH}_4\text{OH}$  (1+1) and hot water and wash into a beaker to a volume of not more than 100 cc. Neutralize with  $\text{HCl}$ , using litmus paper as an indicator, cool, and from a buret add slowly (about 1 drop per second), stirring vigorously, 15 cc. of the magnesia mixture for each decigram of  $\text{P}_2\text{O}_5$  present. After 15 minutes add 12 cc. of  $\text{NH}_4\text{OH}$ . Let stand overnight, filter, wash the precipitate with the dilute  $\text{NH}_4\text{OH}$  until the washings are practically free from chlorides, dry, burn first at a low heat and ignite to constant weight, preferably in an electric furnace, at  $950\text{--}1000^\circ$ ; cool in a desiccator and weigh as  $\text{Mg}_2\text{P}_2\text{O}_7$ . Calculate and report as grams of  $\text{P}_2\text{O}_5$  per 100 cc.

## CALCIUM

DETERMINATION<sup>1</sup>

Using the solution as prepared for the hypophosphite determination, pipet a 20 cc. aliquot into a 400 cc. beaker, dilute to 100 cc., add 2 cc. of  $\text{HCl}$ , 15 cc. of ammonium acetate solution (10%), and a slight excess of saturated  $\text{NH}_4$  oxalate solution. Heat to boiling and allow the precipitate to settle at a temperature just below boiling. Filter hot, wash with 1%  $\text{NH}_4$  oxalate solution, dry, moisten with sulfuric acid, ignite gently, and weigh residue as  $\text{CaSO}_4$ . Calculate and report as grams of  $\text{Ca}$  per 100 cc.

*Collaborative results (grams per 100 cc.)*

ANALYST	$\text{P}_2\text{O}_5$	CALCIUM	$\text{Ca}(\text{H}_2\text{PO}_3)_2$ † FROM $\text{P}_2\text{O}_5$	$\text{Ca}(\text{H}_2\text{PO}_3)_2$ FROM $\text{Ca}$
Calculated results*	2.961	0.826	3.547	3.508
G. M. Johnson	2.987	0.825	3.578	3.504
Food & Drug Adm.	2.978	0.824	3.567	3.500
Chicago	2.883	0.827	3.453	3.512
	2.959		3.549	
Morris L. Yakowitz	2.92	0.861	3.50	3.65
Food & Drug Adm.	2.88	0.861	3.45	3.65
San Francisco				
H. R. Bond	2.955	0.833	3.539	3.538
	2.952	0.830	3.536	3.525
	2.947	0.822	3.530	3.491
Average	2.940	0.835	3.522	3.546
Per cent	99.29	101.08	99.29	101.08

\* Calculation of theoretical results from sample.

†  $\text{H}_2\text{PO}_3$  in sirup calculated as  $\text{Ca}(\text{H}_2\text{PO}_3)_2$ , and included as such in results.

NOTE.—Results in Columns 3 and 4 calculated by Associate Referee from those in Columns 1 and 2.

It is recommended<sup>2</sup> that this method be adopted tentatively.

No report on santonin was given by the associate referee.

<sup>1</sup> *British Pharmacopoeia*, 1932, p. 100.

<sup>2</sup> For report of Subcommittee B and action of the Association, see *This Journal*, 17, 51 (1934).

## REPORT ON ETHER

By W. F. KUNKE (Food and Drug Administration,  
Chicago, Ill.), *Associate Referee*

Last year it was recommended that this subject be continued with special reference given to the influence of essential oils or other volatile substances on the determination of ether.

A review of the literature did not reveal a method for the quantitative separation and determination of ether in a sample containing volatile substances. Petroleum ether will extract essential oils and other volatile substances from a hydro-alcoholic solution that has been saturated with salt, but petroleum ether will also extract ether<sup>1</sup> under these conditions. Mason and McEwan,<sup>2</sup> Formanek,<sup>3</sup> Meyer<sup>4</sup> and Wratschke<sup>5</sup> extract the ether from ether-alcohol-water solution with petroleum ether and the increase in volume of the petroleum ether, after certain corrections have been made, is used as the basis of the estimation of the ether present. Obviously, petroleum ether cannot be used for the problem at hand.

The method for the determination of ether in hydro-alcoholic solution devised by the Associate Referee and recommended last year as a tentative method<sup>6</sup> under certain conditions gave fairly satisfactory results. Briefly, the procedure consists of passing the vapors of ether and alcohol by aspiration for 5 hours at room temperature into sulfuric acid and water (1+1 by volume), which retains the alcohol vapor, but the ether vapor passes through into the 0.5 *N* acid-dichromate solution, where reaction takes place. This method with and without modifications was tried this year. Last year it was found that sulfuric acid and water (1+1 by volume) is a very efficient absorption liquid for alcohol vapor.

With the view to learn whether the volatile substances could be retained in an absorption liquid and prevent the vapor from passing with the ether vapor into the 0.5 *N* potassium dichromate-sulfuric acid solution, experiments were made with various concentrations of sulfuric acid in water, sulfuric acid (95 per cent), aqueous solution of potassium hydroxide (10 grams of KOH per 100 cc.) and a saturated solution of potassium hydroxide in methyl alcohol.

For the work this year twelve of the more commonly used volatile substances, which were considered fairly representative, were selected. The list included oils of wintergreen, sassafras, eucalyptus, cubeb, sandalwood and juniper, creosote, guaiacol, turpentine, menthol, thymol, and camphor.

Experiments (Table 1) were made to determine whether sulfuric acid

<sup>1</sup> U.S.P. X., p. 427.

<sup>2</sup> *J. Soc. Chem. Ind.*, 40, 29 T (1921).

<sup>3</sup> *Chem. Ztg.*, 52, 325 (1928).

<sup>4</sup> *Pharm. Ztg.*, 75, 92 (1930).

<sup>5</sup> *Ibid.*, 75, 319 (1930).

<sup>6</sup> *This Journal*, 16, 357 (1933).

and water (1+1 by volume) could be used as an absorption liquid for vapors of any one or all of the volatile substances. The method reported for ether last year was used except that in most cases the aspiration period was appreciably shortened. Ether was not added to the sample in any experiment.

TABLE 1.—*Experiments with sulfuric acid and water (1+1 by volume) as absorption liquid*

SAMPLE	ADDED TO SAMPLE	ASPIRATION PERIOD	N/2 ACID DICHROMATE SOLUTION CONSUMED		
			NO. 1	CYLINDER NO. 2	NO. 3
	<i>cc. of water</i>	<i>hours</i>	<i>cc.</i>	<i>cc.</i>	<i>cc.</i>
1. 10 cc. of Soln. A*	15	2	5.6	0.9	0.4
2. 10 cc. of Soln. A*	15	1½	3.4	0	0
	20% Alcohol				
3. 0.15 gram of Menthol†	10	3	2.27	0.25	—
4. 0.15 gram of Thymol	10	5	1.38	0	0
5. 0.15 gram of Camphor	10	6	1.08	0	0
6. 0.15 cc. of Creosote‡	10	2	0.3	0	0
7. 0.15 cc. of Guaiacol	10	2	0.25	0	0
8. 0.15 cc. of Oil of Wintergreen	10	2	0.36	0	0
9. 0.15 cc. of Oil of Sandalwood	10	2	0.3	0	0
10. 0.15 cc. of Oil of Sassafras	10	2	1.88	0	0
11. 0.15 cc. of Oil of Cubeb	10	2	3.7	0	0
12. 0.15 cc. of Oil of Juniper	10	2½	5.25	0	0
13. 0.15 cc. of Oil of Eucalyptus	10	2	6.06	0.3	0
14. 0.15 cc. of Oil of Turpentine	10	2	7.75		0

\* A = a composite solution of the 12 volatile substances. This solution contained 0.5 cc. of each liquid and 0.5 gram of each solid volatile substance per 200 cc. of 62% alcohol.

† 3 cc. of an alcoholic solution containing 5 grams of the given substance per 100 cc. was used.

‡ In Experiments 6-14, inc, 3 cc. of a 5% by volume solution of the given substance in alcohol was used.

The quantity of the volatile substance given for each experiment was contained in the aliquot of an alcoholic solution used as indicated in the footnotes to Table 1. In no case did the quantity of alcohol with the sample in the cylinder exceed the safe absorption capacity of the sulfuric acid and water (1+1 by volume) as previously determined and reported.<sup>1</sup> Therefore, the 0.5 N acid-dichromate solution consumed was not due to alcohol vapor.

Experiments (Table 2) were also made to determine whether any one of the various liquids may be used during aspiration to absorb the vapors

<sup>1</sup> *This Journal*, 16, 353 (1933).



of the different volatile substances and alcohol but permit the ether vapor to pass through quantitatively into the 0.5 *N* acid-dichromate solution. It seemed hopeful when it was found that sulfuric acid (95 per cent) will retain all the vapors of the 12 volatile substances (Experiments 1-2-3, Table 2). A saturated solution of potassium hydroxide in methyl alcohol or an aqueous solution of potassium hydroxide (10 grams per 100 cc.) will permit the vapors to pass through (Experiments 4 and 5). However, sulfuric acid (95 per cent) will also absorb ether quantitatively (Experiments 6 and 7).

It appeared to be promising that a certain concentration of sulfuric acid in water (between 62 per cent and 95 per cent  $\text{H}_2\text{SO}_4$ ) might have the desired selective absorption, namely, retain the vapors of alcohol and the volatile substances but permit the ether vapors to pass through.

TABLE 2.—*Experiments with various absorption liquids*

SAMPLE VOLATILE SUBSTANCE	ADDED TO SAMPLE	ABSORPTION LIQUID $\text{H}_2\text{SO}_4$	ASPIRATION PERIOD hours	N/2 ACID DICHROMATE SOLUTION CONSUMED	
				CYLINDER	
				NO. 1	NO. 2
<i>cc.</i>					
1. A*, 10	10 cc. water	95	2	0	0
2. A*, 10	10 cc. water	95	2	0	0
3. A*, 10	10 cc. water	95	2½	0	0
4. A*, 10	10 cc. 40% alcohol	‡	2	3.7	0
5. A*, 10	§	62	1	3.5	0
6. A, 20 ETHER†	0.1753 gram ether	95	5	0	0**
<i>gram</i>					
7. 0.1753	20 cc. water	95	7	0	0**
8. 0.1753	20 cc. 40% alcohol	78	2	0	0**
9. 0.1753	20 cc. 40% alcohol	71	6	2.5	4.5††

\* Composite solution, same as in Table 1, Experiments 1 and 2.

† 5 cc. of alcoholic solution of ether = 0.1753 gram of ether.

‡ 30 cc. of KOH solution (10 grams per 100 cc.) in cylinder No. 2. 35 cc. of  $\text{H}_2\text{SO}_4$ , 62% in each of cylinders 1 and 3.

§ 10 cc. of saturated solution of KOH in methyl alcohol.

\*\* Ether found, none.

†† Ether found, 77.7%.

#### GENERAL REMARKS

If it is assumed that a 0.1851 gram sample of ether in the presence of a volatile substance under conditions given in Table 1 were to be determined quantitatively, the consumption of 0.5 *N* acid-dichromate solution would indicate a possible error ranging from +0.6 to +20 per cent, depending upon what particular volatile substance was present.

A full aspiration period of 5 hours would perhaps increase the errors proportionately. On the other hand, the quantity of essential oil or volatile substance used in each experiment (0.15 cc. or 0.15 gram) is large when compared with a 0.1851 gram sample of ether. A smaller quantity of the volatile substance, perhaps, would cause an appreciably smaller error. However, with the exception of methyl salicylate and thymol, there is no accurate method to determine the quantity of any of the volatile substances which may be present. Consequently, in most cases the determination of ether in the presence of a volatile substance might give a result having a very small or large error, depending upon the volatile substance and the quantity present.

#### SUMMARY

When it is definitely known that the ether sample contains only a comparatively small quantity of methyl salicylate, thymol, camphor, creosote, guaiacol or oil of sandalwood, the procedure developed for the determination of ether and recommended last year as a tentative method gives reasonably accurate results.

The experiments with various concentrations of sulfuric acid in water confirm the conclusion drawn from the results reported last year that sulfuric acid and water (1 + 1 by volume) or 62 per cent  $\text{H}_2\text{SO}_4$  is not only a very efficient absorption medium for alcohol vapor but it also absorbs an appreciable quantity of vapor of a wide variety of volatile substances.

Sulfuric acid, 62 per cent, is the most efficient absorption liquid for alcohol vapor which at the same time permits ether vapor to pass through.

The experimental study does not justify the recommendation of a method for ether in a sample containing an unknown quantity of an essential oil or other volatile substance.

#### RECOMMENDATIONS<sup>1</sup>

It is recommended—

(1) That the method developed and reported last year by the Associate Referee for the determination of ether, which is applicable to ether and aqueous, alcoholic, or hydroalcoholic solutions of ether, be adopted as a tentative method.

(2) That the subject of ether be closed.

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#### REPORT ON BENZYL COMPOUNDS

By JOSEPH CALLAWAY, JR. (U. S. Food and Drug Administration,  
New York, N. Y.), *Associate Referee*

Last year the Associate Referee reported on the determination of small quantities of benzyl alcohol in aqueous solution by the method described

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<sup>1</sup> For report of Subcommittee B and action of the Association, see *This Journal*, 17, 52 (1934).

by Callaway and Reznik.<sup>1</sup> Because it was necessary in this laboratory to examine a number of samples that were believed to contain solid benzyl esters, it was decided first to study the determination of benzyl compounds in tablets based on a determination of the benzyl alcohol present.

In order to use the general method mentioned previously, it was necessary to break up the benzyl ester and distil and collect the benzyl alcohol in aqueous solution free from volatile compounds other than benzyl alcohol. Experiments were made with sodium benzyl succinate and dibenzyl succinate. After a few trials it was found that these products were easily saponified by refluxing with aqueous alkali and that the benzyl alcohol freed from them could be distilled over and collected and the amount determined from the immersion refractometer reading of the distillate. To test a method based on this procedure three samples were prepared for collaborative work.

*Sample A* contained 88.2 per cent of benzycin (sodium benzyl succinate), 10 per cent of starch, and the remainder talc. The sodium benzyl succinate used was the ordinary commercial product known as benzycin and was found to contain 21.2 per cent of moisture. The calculated amount of benzyl alcohol present in the prepared sample was 32.6 per cent.

*Sample B* consisted of a mixture of dibenzyl succinate, starch, and talc. The dibenzyl succinate contained only about 1 per cent of moisture. It was otherwise assumed to be pure, therefore the calculated amount of benzyl alcohol in the prepared sample was taken as 63.8 per cent.

*Sample C* consisted of commercial tablets supposed to contain 5 grains of dibenzyl fumarate per tablet. On the assumption that the material extracted by chloroform from the ground sample was pure dibenzyl fumarate, the calculated amount of benzyl alcohol in *Sample C* was 42.6 per cent.

As noted, it was not easy to obtain satisfactory samples for collaborative work because the purity of the commercial products was not known. *Sample C*, in addition to dibenzyl fumarate, contained some aromatics. It was therefore believed to be desirable to provide a means of removing volatile aromatic compounds, as numerous commercial preparations contain small quantities of such products for flavoring purposes. The following directions were therefore sent out to collaborators with the samples:

Take a sample estimated to yield 2-3 grams of benzyl alcohol. If the first determination shows that the sample taken yields less than 1.5 grams of benzyl alcohol, repeat the determination, using a sufficiently large sample to yield 2.5 grams of benzyl alcohol. If the odor of the ground sample shows that it contains a volatile oil, remove the oil by the following procedure: Place the sample in a round-bottomed distilling flask of about 300-500 cc. capacity, add a few glass beads, attach a still-head, such as is used in the Clevenger apparatus for determining volatile oils [*This Journal*, 17, 70 (1934)], add 100 cc. of water, make acid to litmus paper with dilute

<sup>1</sup> *This Journal*, 16, 285 (1933).

sulfuric acid, and reflux until odor of distillate indicates removal of volatile oils. Continue to reflux and remove portions of the distillate until the residue is concentrated to about 50 cc. Now add 20 cc. of 25% NaOH, attach to an efficient and scrupulously clean reflux condenser, adjust the flame so that the liquid just boils, and reflux for an hour.

If no volatile oil is indicated in the original sample, transfer the sample directly to the distilling flask, add 50 cc. of 10% NaOH, and reflux for an hour as directed above.

Cool, and wash down the condenser, making the volume up to about 150 cc. Then distil, using a straight condenser, which must also be scrupulously clean. Collect about 100 cc. in a 200 cc. volumetric flask, remove flame, and allow the flask to cool. Add 50 cc. of water, redistil, and collect an additional 50 cc. of distillate. Again allow the flask to cool and repeat the procedure of adding 50 cc. of water and distilling. Make total volume of distillate up to 200 cc. with water.

*Note.*—If such excessive foaming takes place during refluxing or distilling that the operation cannot be satisfactorily carried out, control can be effected with only a slight loss of benzyl alcohol by blowing a slight current of air against the top of the foaming liquid. An apparatus similar to that for crude fiber determination (*Methods of Analysis, A.O.A.C.*, 1930, 280) may be used. If the current of air is used during the distillation, the end of the condenser should fit well into a flask surrounded with ice.

Determine the specific gravity of the distillate at 20°/20° and immersion refractometer reading at 20°C. Calculate the benzyl alcohol in the distillate from the refractometer reading, using the formula "grams of benzyl alcohol/100 cc. of solution =  $(r - 14.40) \times 0.193$ ," where " $r$ " is the refractometer reading at 20°C. For quantities of benzyl alcohol up to 3%, the specific gravity should be between 1.000 and 1.002. If specific gravity indicates that the distillate contains some other volatile materials than benzyl alcohol and water, carry out the oxidation procedure described last year [*This Journal*, 16, 288 (1933)].

The following results were reported by the collaborators:

COLLABORATORS	SAMPLE A		SAMPLE B		SAMPLE C	
	(1)	(2)*	(1)	(2)	(1)	(2)
Allison, Food & Drug Adm., New York	28.4†	28.0	63.0†	60.0	37.5†	36.5
	28.4	28.4	62.0	59.0	38.5	38.0
Reznek, Food & Drug Adm., New York	30.8	30.0	61.2	56.3	41.9†	36.5
	31.6	30.0	—	57.1	40.8	38.0
Yakowitz, Food & Drug Adm., San Francisco	28.93†	28.89	62.06	62.73	39.84†	39.86
	28.96	29.42	62.14	63.01	40.37	39.89
Cannon, Food & Drug Adm., Chicago	30.48	—	51.2	—	41.1†	—
	30.48	—	51.5	—	41.1	—
Hoshall, Food & Drug Adm., Baltimore	30.9	29.7	51.2	53.8	38.6†	38.8
	30.0	43.5	43.5	41.7	39.6	39.0
			62.0	60.8		

\* (1) Grams per 100 cc. benzyl alcohol calculated from immersion refractometer reading. (2) Grams per 100 cc. benzyl alcohol calculated from benzoic acid by oxidation.

† Volatile oil removed.

#### COMMENTS

*Cannon.*—No difficulty was encountered in following the method as given. There was a tendency to frothing in the case of Sample C, but it was not deemed

necessary to use a current of air. Could not paraffin be used at this point to control frothing?

*Hoshall.*—The results for this sample (B) are given to show the difficulties of the determination when other volatile oxidizable substances are apparently present, and *NOT* as analytical results of the benzyl alcohol content. Our experience with benzoic acid determination indicates that a chloroform solution may be taken to dryness at room temperature, with the aid of a fan, without appreciable loss. The present method recommends a somewhat involved procedure.

*Yakowitz.*—Each sample was distilled in duplicate. The figures refer to the values found on these duplicates and are consistent.

The only sample to show any frothing was C. I overcame this by using a 500 cc. flask with a long neck, 5 inches, and inserting a small loose plug of glass wool in the neck. Sample C was peculiar also in that it contained a small quantity of volatile solid which formed a skin on the surface of the distillate and which did not dissolve on shaking. It didn't interfere with the oxidation or refractometer reading.

The method is easy and with care should yield consistent results. Especial care should be taken in measuring the refractive index. The immersion refractometer should be carefully checked as to its water reading and the temperature must be correct. As the total difference between the reading of a distillate and pure water is approximately six Zeiss units, an error of one-tenth unit means an error of almost 2 per cent.

It will be seen that all the results show somewhat less benzyl alcohol than the calculated amount. As explained previously, however, the calculated amounts are based on assumptions as to purity that may not have been entirely correct. The agreement between analysts is fairly good. It is believed that this method will yield reasonably accurate results on benzyl alcohol in ordinary combination and in solid esters such as are found in tablets.

It is recommended<sup>1</sup> that the work on benzyl compounds be extended to cover the determination of benzyl alcohol in benzyl benzoate and also the identification of the different benzyl esters ordinarily encountered.

## REPORT ON SMALL QUANTITIES OF MORPHINE IN SIRUP

By E. O. EATON (U. S. Food and Drug Administration,  
San Francisco, Calif.), *Associate Referee*

The sirups used contained 0.048 gram of morphine sulfate, 5 H<sub>2</sub>O per 100 cc.; Sirup of White Pine Comp., Fl. Ex. Ipecac Sol., and Simple Sirup. The samples were submitted to four collaborators. The method follows:

Shake the bottle well and transfer 50 cc. to a 150 cc. pear-shaped separatory funnel. Add a few drops of 10% ammonia water to insure a weak alkaline reaction; test with litmus paper. Extract the total alkaloids with a mixture of chloroform and alcohol (9:1). (About seven 25 cc. portions are necessary, depending on care of separating the solvent and length and violence of each shake-out.) Combine the

<sup>1</sup> For report of Subcommittee B and action of the Association, see *This Journal*, 17, 52 (1934).

solvent and wash with 5 cc. of water. Run through chloroform-wetted cotton. Evaporate the solvent. (If the sirup is known to carry only pure morphine alkaloid or its salt, and no other alkaloid, this residue may be dissolved in alcohol, filtered, washed, and titrated.) Dissolve in 2 cc. of 5% hydrochloric acid on water bath, covering beaker to insure complete solution. Add 20 cc. of water and transfer to a separatory funnel. Make alkaline with 5 cc. of 5% potassium hydroxide solution and exhaust with three 20 cc. portions of chloroform followed by two 20 cc. portions of petroleum ether. (Removal of non-phenolic alkaloids and chloroform.) Combine immiscible solvents and wash with 5 cc. of water. Discard the solvent and add wash water to main aqueous solution.

Render the aqueous solution acid with 5% hydrochloric acid and then just alkaline with a few drops of 10% ammonia and extract with three 20 cc. portions of petroleum ether. (Removal of petroleum ether-soluble phenolic alkaloids.) Wash the combined petroleum ether with 5 cc. of water. Discard the petroleum ether.

Add the wash water to the main aqueous solution. Saturate with salt.

Extract the morphine completely with seven 25 cc. portions of chloroform and alcohol (9:1) mixture. Combine the solvent. Wash with 5 cc. of water and run solvent through a plug of chloroform-saturated cotton. Evaporate the solvent. Dissolve the residue in 5 cc. of neutralized alcohol in a covered beaker by aid of heat on steam bath. Add an excess of 0.02 *N* sulfuric acid and back titrate with 0.02 *N* alkali, using methyl red indicator.

Each cc. of 0.02 *N*  $\text{H}_2\text{SO}_4$  = 0.0076 gram of morphine sulfate + 5  $\text{H}_2\text{O}$ .

Collaborators report grams per 100 cc. morphine sulfate: 5  $\text{H}_2\text{O}$ :

*Irwin S. Shupe*.—0.046; 0.044; 0.046.

*Rupert Hyatt*.—0.0401; 0.0418.

*E. O. Eaton*.—0.0426; 0.0424.

*Baltimore Station*.—0.0442; 0.0439.

Average recovery: 93.7 per cent

Hyatt also reported that the method was apparently satisfactory, and Shupe that he considered a larger titration volume would be preferable. Baltimore Station reports in part criticism, which has been incorporated in the rewritten paper and follows:

If 25 cc. of chloroform alcohol mixture is used in the initial shake-out, as is recommended, then emulsification occurs even with very light shaking. However, if 50 cc. is used, the two immiscible liquids may be shaken as hard and as long as may be desired without emulsification. With 50 cc. portions, five or six extractions will remove all the alkaloid.

#### SUMMARY

These results are fairly satisfactory in view of the complexity of the mixture submitted for analysis. Possibly some improvement in the technic of the method may show more uniform results.

It is thought<sup>1</sup> that further collaborative work should be done next year on a slightly modified procedure.

No report on guaiacol was given by the associate referee.

<sup>1</sup> For report of Subcommittee B and action of the Association, see *This Journal*, 17, 52 (1934).

REPORT ON BROMIDE-BROMATE  
VOLUMETRIC SOLUTIONS

By H. WALES (U. S. Food and Drug Administration,  
Washington, D. C.), *Associate Referee*

Last year question was raised in regard to the necessity of using a large excess of bromide in the standard bromide-bromate solution as is now specified by the U.S.P. and A.O.A.C. methods, and also as to the need for more than one such solution, particular comment being made concerning the solution specified for the titration of acetanilid.

## DISCUSSION

The method for acetanilid and caffein given in *Methods of Analysis*, A.O.A.C., 1930, specifies that the bromide-bromate solution shall contain 15 grams of potassium bromate and 100 grams of potassium bromide in a liter of water. This solution is also specified for acetanilid in most combinations. A solution containing 3 grams of potassium bromate and 50 grams of potassium bromide in a liter of water is specified for the determination of acetanilid in acetanilid and acetphenetidin, and for procaine, thymol, salicylic acid and salol. This is the "tenth normal bromine solution" of the U.S.P. The first-mentioned of these solutions represents one containing bromate and bromide in the molecular ratio of 1:9. The second solution is approximately 1:23.

According to theory 5 moles of bromide are required for each mole of bromate for the reaction,  $\text{HBrO}_3 + 5 \text{HBr} = 3 \text{Br}_2 + 3 \text{H}_2\text{O}$ .

In an effort to learn why these different solutions were recommended reference was made to the original articles. This led to the discovery that in many cases the standard solutions in *Methods of Analysis* differed from those described in the original papers. For example, N/7 bromine solution was originally specified for salol instead of the U.S.P. solution<sup>1</sup> called for at the present time. The original work on the determination of acetanilid when mixed with caffein<sup>2</sup> called for a bromine solution prepared by saturating a solution of 50 grams of potassium hydroxide with bromine, boiling to expel the excess bromine, and diluting to 1 liter. This method was published in the first (1920) edition of *Methods of Analysis*. The second edition (1925) called for the U.S.P. solution of 3 grams of bromate and 50 grams of bromide per liter, and the third edition calls for 15 grams of bromate and 100 grams of bromide per liter. The molecular ratios of bromate to bromide in the three solutions provided in the three editions are approximately 1:5, 1:23 and 1:9. In terms of available bromine these solutions are approximately 0.8 N, 0.1 N and 0.5 N. A search through the proceedings of the A.O.A.C. for the period covered by these three edi-

<sup>1</sup> *J. Ind. Eng. Chem.*, 7, 681 (1915).

<sup>2</sup> U. S. Dept. Agriculture, Bur. Chemistry Bull., 132, p. 197.

tions failed to show any reason for the changes in the strengths of the solutions or any suggestion that such changes be made.

The first mention of the standard bromine solution in the U.S.P. appeared in the seventh edition and has been retained in subsequent editions. It calls for 3 grams of sodium bromate and 50 grams of sodium bromide (or 3.2 grams of potassium bromate and 50 grams of potassium bromide) in 1 liter. A search through the circulars of the Revision Committee for U.S.P. VII revealed a pamphlet, which was apparently issued as Circular 96, entitled "Reagents and Volumetric Solutions Proposed for the U. S. Pharmacopoeia together with some Specimens of the Text Proposed, Published by the Committee of Revision and Publication of the Pharmacopoeia of the U. S. of America, St. Louis, 1892." This pamphlet directed that a solution be made by dissolving 16 grams of sodium bromate and 62 grams of sodium bromide (or 18 grams of potassium bromate and 70 grams of potassium bromide) in 800 cc. of water and adjusting the strength by titration against standard sodium thiosulfate solution until it would correspond to a 0.6 *N* solution towards phenol. Subsequent circulars relating to the proposed volumetric solution made no reference to this bromine solution. However, in a package labeled "Reports of Committees" there was located a manuscript copy of the carbolic acid monograph which bore the notation, "The bromine solution on page 17 of reagents should be adjusted so that 1 cc. of it corresponds to 2 cc. of hyposulphite or it may be 1 to 4." This suggestion was not followed, and the seventh edition was published with essentially the same proportions of bromide and bromate as are given in the present U.S.P. There appears to be the same lack of background for the use of this solution as for the solutions given in *Methods of Analysis*, A.O.A.C.

In addition to the variable excess of bromide specified it was noticed that the various methods requiring the use of this titrating agent provide in some cases for direct titration to produce a yellow coloration, while in other instances a measured excess of the bromine is added and this excess determined with standard thiosulfate solution after addition of potassium iodide. It was therefore decided to investigate the two methods of titration as well as the question of the excess bromide required in the reagent.

#### EXPERIMENTAL

Three solutions were prepared.

No. I.—A solution of 50 grams of potassium hydroxide in water was saturated with bromine, boiled to expel the excess of bromine, and diluted with water to 1 liter.

No. II.—3 grams of potassium bromate and 50 grams of potassium bromide were dissolved in water to make 1 liter.

No. III.—3 grams of potassium bromate and 12 grams of potassium bromide were dissolved in water to make 1 liter (theory for 0.1 *N* = 2.7837 g.  $\text{KBrO}_3$  and 9.9186 g.  $\text{KBr}$ ). The only essential difference between I and III is that of normality. As the solution now specified in *Methods of Analysis* for the determination of acet-



anilid in mixtures of acetanilid and caffen falls between I and II in both normality and in excess of bromide it was not regarded as essential to give it any study. The strengths of the three solutions were determined by titration against standard sodium thiosulfate as provided in the U.S.P. and on page 446 of *Methods of Analysis*, A.O.A.C., 1930. Their strengths were also determined by titrating weighed quantities of pure acetanilid as specified on page 439 of the same edition. The two methods of standardization give the same results.

The three solutions were used for the analyses of acetanilid, phenol, thymol, salicylic acid, and procaine hydrochloride according to the official methods, and all three gave the same results. Since it was rather difficult to determine the end point with the weaker solutions when the official method for acetanilid was followed the back titration method specified for the other products was tried. This method gave results identical with those obtained by direct titration, and it has the advantage of giving a more definite end point.

No actual collaborative work was requested on this problem. Letters were sent to several chemists experienced in the determination of acetanilid. Their comments are summarized below.

*T. F. Pappe, Baltimore Station, F. & D. Administration*, sees no reason why the bromide-bromate solution should be standardized against acetanilid and has used a solution standardized against thiosulfate. He believes two strengths of solutions are necessary on account of the varying proportions of acetanilid and other ingredients in mixtures.

*E. O. Eaton and Morris Yakowitz, San Francisco Station, F. & D. Administration*, use the U.S.P. bromide-bromate solution, standardized against thiosulfate for all titrations. They state that they obtain the same standardization using acetanilid and know of no reason for using an excess of bromide. They favor the back titration.

*E. L. Anderson, New York Station, F. & D. Administration*, uses 0.1 N and 0.5 N bromine solutions containing only a slight excess of bromide. He states that the solution may be standardized against either thiosulfate or acetanilid. He sees no objection to the back titration, but has no difficulty in detecting the end point with the present method.

#### SUMMARY AND RECOMMENDATIONS<sup>1</sup>

Three bromide-bromate solutions differing both in normality and ratio of the two salts have been official in the three editions of *Methods of Analysis*, A.O.A.C. The method for acetanilid as originally proposed provided for titration with a solution containing potassium bromide and potassium bromate in a molecular ratio of 5 to 1. The use of an excess of bromide has no justification.

It is recommended—

(1) That the method for preparing standard bromide-bromate solution. [5(a), p. 439<sup>2</sup>] be amended to read "Dissolve 14 g of KBrO<sub>3</sub> and 55 g of

<sup>1</sup> For report of Subcommittee B and action of the Association, see *This Journal*, 17, 52, 78 (1934).

<sup>2</sup> *Methods of Analysis*, A.O.A.C., 1930.

KBr in  $\text{H}_2\text{O}$ . Dilute to 1 liter and standardize the solution against recrystallized and dried acetanilid according to 4 (b),\*\* beginning with the expression "Add 10 cc. of  $\text{H}_2\text{SO}_4$  (1+9)."

(2) That par. 5 (a) be further amended by adding the following expression: "The solution may also be standardized by the following method: Transfer 10 cc. of the bromide-bromate solution to a glass-stoppered flask and add 25 cc. of  $\text{H}_2\text{O}$ , 5 cc. of KI solution and 5 cc. of HCl. Shake thoroughly and titrate the liberated I with 0.1 N  $\text{Na}_2\text{S}_2\text{O}_3$  solution, using starch solution as indicator 3 (e), p. 35."

(3) That the method for the preparation of standard bromide-bromate solution, 25 (c), p. 446, be amended by deleting the expression "50 g" in the second line of the paragraph and substituting the expression "12 g."\*

(4) That the last sentence in the first paragraph of 7 (b), p. 441, be deleted and the following statement added: "Each cc. of 0.5 N bromide-bromate solution equals 0.01126 g of acetanilid."

(5) That 7 (b) be further amended by adding a new paragraph to read: "(a) Acetanilid may also be determined by adding an excess of the standard bromide-bromate solution to the solution of anilin sulfate obtained as in b and titrating back the excess with 0.1 N  $\text{Na}_2\text{S}_2\text{O}_3$  after the addition of 5 cc. of KI solution and starch solution as indicator [VI, 3 (e)]. Each cc. of 0.1 N bromide-bromate solution = 0.002252 g of acetanilid."

(6) That par. 19 (b), p. 445, be amended by adding after the expression "0.1 N bromide-bromate solution" the expression "25 (c)."

The Associate Referee on Rhubarb and Rhaponticum presented a report illustrated by lantern slides. This report will be published elsewhere. See also remarks of the Referee on Drugs.

## REPORT ON TETRACHLORETHYLENE

By G. M. JOHNSON (U. S. Food and Drug Administration,  
Chicago, Ill.), *Associate Referee*

No collaborative work has been done on the subject of tetrachlorethylene. However, Elliott<sup>1</sup> reported in preliminary work at the 1932 meeting that 93.5 per cent saponification was obtained with a concentrated solution of potassium hydroxide in methyl alcohol. After considerable work this year, the method was abandoned as no higher results were obtained.

Tetrachlorethylene ( $\text{C}_2\text{Cl}_4$ ) is a heavy colorless liquid with a characteristic odor miscible with alcohol and most organic solvents but practically insoluble in water. According to the International Critical Tables,

\* It will be noted that in both cases a slight excess of potassium bromide is provided. This is because U.S.P. salt need contain only 93.6 % of KBr, that is 98.5 % of KBr after allowance for 5 % of water.

<sup>1</sup> *This Journal*, 16, 383 (1933).

1927, the density is 1.623 20°/4°C. and the boiling point 120.8°C. (760 mm.). It is stated that the principal drug use of this compound is for the treatment of hook worm by veterinarians.

The material for the work this year was prepared by double distillation from a commercial product. The boiling point of the final distillate was 121.4°C. (760 mm.) and the density 1.625 20°/4°C. The refractive index was 1.504 at 20°C. It was free from chlorine and chlorides, gave no residue on evaporation, and was considered sufficiently pure for this investigation.

A sample consisting of this double distilled tetrachlorethylene, together with directions for the method, was submitted to the collaborators.

The method is essentially the modified Stepanow method as described by Landis and Wichmann.<sup>1</sup> It consists of refluxing the tetrachlorethylene with xylene and amyl alcohol in the presence of metallic sodium and the subsequent determination of the chloride, either volumetrically or gravimetrically.

The method has been published [*This Journal*, 17, 78 (1934)].

The reports and comments of collaborators are as follows:

COLLABORATOR	VOLUMETRIC	GRAVIMETRIC
	per cent	per cent
W. F. Kunke, U. S. Food & Drug Adm., Chicago	100.1	—
	100.3	
	99.6	
Morris L. Yakowitz, U.S. Food & Drug Adm., San Francisco	—	100.0
		100.5
F. C. Sinton, U.S. Food & Drug Adm., New York	99.6	—
	99.6	
	99.1	
I. S. Shupe, U.S. Food & Drug Adm., Chicago	100.1	—
	99.8	
	99.2	
H. R. Bond, U.S. Food & Drug Adm., Chicago	99.6	
	99.6	
G. M. Johnson	99.1	99.4
	98.9	
	98.9	

#### COMMENTS

*W. F. Kunke.*—Numerous experimental weighings of xylene under conditions similar to those under which the tetrachlorethylene samples were weighed by dif-

<sup>1</sup> *Ind. Eng. Chem. Anal. Ed.*, 2, 394 (1930).

ference, lead me to believe that results higher than 100% are mainly due to possible loss of xylene by evaporation between weighings. Consequently, assuming such a loss, the recorded weight of tetrachlorethylene is less than the actual and result of recovery is slightly high. The procedure works smoothly and as a practical method it appears satisfactory.

*Morris L. Yakowitz.*—The method is simple and straightforward, and no difficulties were encountered.

*F. C. Sinton.*—The method appears to be quite satisfactory. No difficulties were encountered in the assay, and it is not necessary to offer any criticism.

*I. S. Shupe.*—An error in weighing the small quantity of sample is easily made because of the volatility of xylene and tetrachlorethylene.

*H. R. Bond.*—No difficulties were encountered in the procedure. No adverse comment is offered.

The average of seventeen determinations is 99.6 per cent. From this mean the maximum deviation is about 1 per cent. As noted by two of the collaborators, unless due care and precaution are exercised in the weighing of the sample an error may be introduced. However, only a few of the collaborators obtained high results. The correspondence with the collaborators indicates that the chemical reaction upon which the determination depends goes to completion.

#### RECOMMENDATIONS<sup>1</sup>

It is recommended—

- (1) That the method submitted be adopted as tentative.
- (2) That work be undertaken on mixtures containing tetrachlorethylene.

No report on hexylresorcinol was given by the associate referee.

### REPORT ON CHEMICAL ASSAY FOR ERGOT ALKALOIDS

By C. K. GLYCART (U. S. Food and Drug Administration,  
Chicago, Ill.), *Associate Referee*

The highly satisfactory results obtained by the three collaborators last year warranted the continuation of the study of the chemical assay for ergot alkaloids recently devised by M. I. Smith.<sup>2</sup>

Two British investigators, Allport and Cocking,<sup>3</sup> after a critical examination of the colorimetric reaction of paradimethylamino-benzaldehyde and sulfuric acid reagent with ergot alkaloids, reported in 1932 that their modification of the Smith reagent, which contains a minute quantity of ferric chloride, was capable of developing a maximum intensity of the

<sup>1</sup> For a report of Subcommittee B and action of the Association, see *This Journal*, 17, 52 (1934).

<sup>2</sup> *Public Health Reports*, 45, 1468 (1930).

<sup>3</sup> *Quart. J. Pharm. Pharmacol.*, Sept. 13, 1932, 11.

blue color almost immediately in the dark. It is apparent that the light factor is eliminated. The modified reagent contains 65 per cent of sulfuric acid by volume; thus chilling the solution to prevent charring of the alkaloids by contact with concentrated sulfuric acid is eliminated. It was also shown that it is of utmost importance that the ether reagent contain no peroxide as this impurity interferes with the development of the blue color.

According to Smith and Stohlman,<sup>1</sup> there is urgent need for a uniform standard of reference for ergot. A fluidextract of ergot distributed by the U. S. Food and Drug Administration in ampuls is the standard specified by the U.S.P. Ergotoxine ethanesulfonate has been adopted recently by the British Pharmacopoeia. Ergotamine tartrate is the standard advocated by Smith.

As these standard solutions tend to change even when stored at low temperatures, the feasibility of the use of a permanent glass standard for colorimetric comparison, based on the maximum color intensity produced by the total alkaloids from a given quantity of U.S.P. standard fluidextract of ergot, was given consideration last year.

In the preliminary work this year J. H. Cannon of the Chicago Station devised a standard blue solution prepared from coal tar dyes referred to ergotamine tartrate standard solution and Allport-Cocking reagent. F. A. Upsher Smith, Minneapolis, Minn., recently proposed a chemical standard consisting of a 0.67 per cent crystalline copper sulfate in ammoniacal solution.<sup>2</sup> Considering the importance of the subject the Associate Referee prefers to make no definite statement at this time in relation to permanent standards.

The work this year was a comparative study of the Erlich-Smith and the Allport-Cocking reagents. The material sent to the collaborators consisted of fluidextract of ergot for assay, a standard solution containing 0.01 per cent ergotamine tartrate, Erlich-Smith reagent, Allport-Cocking reagent, and a specimen of the standard blue dye solution devised by Cannon.

The directions for the method follow:

#### COLORIMETRIC ASSAY FOR ALKALOIDS OF ERGOT

##### REAGENTS

- (a) *Ethyl ether*.—U.S.P. (peroxide free).
- (b) *Tartaric acid solution*.—1 %.
- (c) *Erlich-Smith reagent*.—Dissolve 2.49 grams of purified paradimethylaminobenzaldehyde in 1 liter of concentrated  $H_2SO_4$ .
- (d) *Allport-Cocking reagent*.—Dissolve 1.25 grams of purified paradimethylaminobenzaldehyde in a solution containing 650 cc. of concentrated  $H_2SO_4$ , 0.05 gram of ferric chloride, and sufficient water to make 1 liter.

<sup>1</sup> *J. Pharmacol.*, **40**, 77 (1930).

<sup>2</sup> *J. Am. Pharm. Assoc.*, **23**, 25 (1934).

(e) *Ergotamine tartrate standard solution*.—0.01 %. With the aid of an excess of tartaric acid, dissolve sufficient ergotamine tartrate, accurately weighed, gradually adding water, to yield a 0.01 % solution of ergotamine tartrate in a 0.05 % solution of tartaric acid.

#### EXTRACTION OF ALKALOIDS

Pipet 5 cc. of the fluidextract at 20°C. into a separatory funnel and dilute with 50 cc. of water. Add 2 cc. of  $\text{NH}_4\text{OH}$  (1+10), or until distinctly alkaline to litmus paper. Extract with ether, using 40, 25, 20, 15 cc. portions, or until the alkaloids are removed completely. Combine the ether extractions in a separatory funnel, wash at least three times with 25 cc. portions of water and three drops of  $\text{NH}_4\text{OH}$  to remove the yellow pigments, and finally wash twice with water to remove the excess of alkali. Shake the ether with an aqueous 1 per cent tartaric acid solution, using 10, 10, 10, and 5 cc. portions, respectively, or until alkaloids are removed completely. Evaporate the combined acid solution on a water bath in a current of air to remove the ether, transfer the solution to a 25 cc. volumetric flask, and make to volume.

#### DETERMINATIONS

*No. 1.—Erllich-Smith reagent*.—Pipet 1 cc. of the standard solution of ergotamine tartrate at 20°C. to a clear glass colorimetric cup or test tube, add 1 cc. of water, place in ice water, and add dropwise, with stirring, 1 cc. of the reagent. Pipet 1 cc. of the ergot solution to a second cup or test tube and add the water and the reagent in a similar manner. Remove from bath, place if possible in direct sunlight for 30 minutes or in diffused daylight of a cloudy day for 2 hours or longer, or until maximum intensity of a clear violet blue color develops. Read in a colorimeter (a Klett bi-colorimeter with microplungers and cups is suitable). Repeat the comparison if necessary with aliquots of the alkaloidal solutions to produce about the same color intensities. Calculate the percentage of total alkaloids of ergot as ergotamine tartrate. 1 cc. of standard solution contains 0.0001 gram of ergotamine tartrate.

*No. 2.—Allport-Cocking reagent*.—Pipet 1 cc. of the standard ergotamine tartrate solution at 20°C. to a glass colorimeter cup or test tube and add with stirring 2 cc. of the reagent. Pipet 1 cc. of the ergot solution to a second cup or test tube and add with stirring 2 cc. of the reagent. Allow to stand for at least half an hour and read in a colorimeter. Repeat the comparison if necessary with aliquots of the alkaloidal solutions to produce about the same color intensities. Calculate the percentage of total alkaloids of ergot as ergotamine tartrate. 1 cc. of the standard solution contains 0.0001 gram of ergotamine tartrate.

The results and comments of the collaborators follow:

#### COLLABORATIVE RESULTS

*J. H. Cannon, U.S. Food & Drug Adm., Chicago*

RESULTS	(8-11-33) A.-C. REAGENT g./100 cc.	(8-11-33) SMITH REAGENT g./100 cc.	(8-11-33) BLUE DYE
Total alkaloids in fluidextract as ergotamine tartrate	0.054 0.055 0.057	0.057	Colorimeter readings— Standard 15 Blue dye 15

(1) A Klett bio-colorimeter with micro plungers and cups and fitted with electric lamp was used. Colors were not so easily matched by the artificial light as by daylight, hence daylight was used.

(2) The blue dye was prepared from the following: Soluble blue, 0.0186 gram; light green SF yellowish, 0.0091 gram; amaranth, 0.0032 gram; and water to make, 1000 cc.

*M. B. Moore, Abbott Laboratories, N. Chicago.*—The materials were placed in a refrigerator as soon as received. Assay was carried out on August 31, 1933. A Klett bio-colorimeter was used, the color being developed in test tubes with twice the volumes suggested. The ergotamine tartrate standard and the sample (duplicates) were compared with the standard blue color.

*Ehrlich-Smith reagent:* Sample (1) 0.054 g./100 cc.; sample (2) 0.057 g./100 cc.

*Allport-Cocking reagent:* Sample (1) 0.05 g./100 cc.; sample (2) 0.05 g./100 cc.

The standard blue color was very satisfactory for the samples prepared with Allport-Cocking reagent, but those prepared with the Ehrlich-Smith reagent had a pinker tone and were harder to match. Comparisons of the unknown with the ergotamine tartrate, however, gave approximately the same ratio.

If it can be shown to give as close correlation with biological assays, the Allport-Cocking reagent should be preferable. It has a great advantage in that it does not depend upon a source of light. In our experience, it has seemed that the shade and even the final intensity of color with the Ehrlich-Smith reagent may depend upon the source of light used. The samples mentioned were developed in bright afternoon sunlight.

*Irwin S. Shupe, U.S. Food & Drug Adm., Chicago*

	DATE OF ANALYSIS	METHOD	ALKALOIDS OF ERGOT CALCULATED TO ERGOTA- MINE TARTRATE g./100 cc.
A.O.A.C. fluidextract	9- 9-33	E-S	0.058
A.O.A.C. fluidextract	9- 9-33	A-C	0.056
Same fluidextract stored in refrigerator	10-20-33	A-C	0.050
Same fluidextract stored at room temperature since 9-6-33	10-20-33	A-C	0.030

(1) A stored solution of ergotamine tartrate containing mold, prepared 8-11-33, showed no deterioration on 10-20-33 when compared with a newly prepared standard.

(2) Alkaloids extracted from the fluidextract showed no deterioration when evaporated to dryness in presence of excess tartaric acid.

(3) The standard ergotamine tartrate solution showed deterioration from heating. A portion evaporated to dryness showed about 7 per cent deterioration.

(4) About 6 per cent of the total amount of alkaloids was recovered from the five 25 cc. portions of wash water used to remove pigments from the ether extract.

(5) In preparing the A-C reagent, a quantity of ferric chloride solution was added to correspond to 0.05 gram of  $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$  per liter of reagent. The method specifies "0.05 gram of ferric chloride."

(6) The following usual procedure of testing for complete extraction in alkaloidal determinations was used:

Make an additional extraction with the solvent and evaporate the solvent in a separate beaker; dissolve the residue in 1 cc. of water and test with the reagent (A-C or E-S) for formation of blue color. The color can be compared to a standard and the determination made quantitative.

*M. I. Smith, United States Public Health Service, Washington, D.C.*—The material was received at the laboratory during my absence. It was kept at rather high room temperature until August 21. It is not probable that the fluidextract deteriorated in the interim, but the standard ergotamine tartrate had become moldy and I was obliged to use my own standard.

The results of the chemical assay of the fluidextract of ergotamine tartrate obtained by using the E-S reagent were: (1), 0.053 g./100 cc.; and (2) 0.054 g./100 cc. A check by the Broom-Clark method gave in one experiment a value somewhat greater than 0.5, and in another somewhat less than 0.6 mg. per cc.

I am glad you stress the purity of ether. Owing to the recent economy campaign we got some cheap ether, labeled "USP not for anesthesia" but I could get no results worth recording and wasted a considerable amount of the A-C reagent. I then switched to ether anhydrous, the only other ether we happened to have in the laboratory, and I had no further difficulty.

One test of the fluidextract by the A-C reagent gave a value of 0.062 gram of ergotamine tartrate, some 15% higher than the result with the E-S reagent. Unfortunately I did not have enough reagent to repeat the test.

A comparison of the E-S and the A-C reagents on several solutions of ergotamine tartrate ranging from .06 to .10 mg. seems to indicate somewhat higher values for the A-C reagent, but the difference was not greater than 10%. On the whole, I am favorably impressed with the A-C reagent, as it appears to be independent of light. I should like to emphasize again the optimum conditions with the E-S reagent, 20 to 30 minutes of direct sunlight, or if this is not available, 20 to 30 minutes' exposure to carbon-arc lamp at a distance of about 15 cm. A poor source of light, while it may be compensated for in part by lengthening the period of exposure, will nevertheless give somewhat irregular and usually low values.

Your contribution towards a permanent standard is splendid I think. Several tests of this standard in reference to ergotamine tartrate, with either the E-S or A-C reagent, gave concordant values, the equivalent of nearly 0.06 mg. of ergotamine tartrate. The colors were not precisely identical, but the readings were quite satisfactory.

I am not convinced, however, as to the wisdom of a permanent artificial standard. I see no difficulty with the ergotamine or ergotoxine standard; both can be used in any of the physiological methods of assay and are to be preferred in the chemical assay as well. Any irregularity in the proportionality of the color in the ergotamine or ergotoxine standard should at once be a warning to the operator that the conditions are not right.

*Wm. T. McClosky, U. S. Food and Drug Adm., Washington, D.C.*—The following is a summary of our report:

(1)—E-R reagent mg. per cc.	(2)—A-C reagent mg. per cc.	(3)—E-R reagent mg. per cc.
A—0.5154	A—0.5304	A—0.6112
B—0.5454	B—0.5245	B—0.6012
Av.—0.5304	Av.—0.5274	Av.—0.6062
(4)—A-C reagent mg. per cc.	(5)—A-C reagent mg. per cc.	(6)—E-R reagent mg. per cc.
A—0.6610	A—0.6820	A—0.4709
B—0.6909	B—0.6525	B—0.4496
Av.—0.6759	Av.—0.6672	Av.—0.4602



(1) Checked against standard prepared with the E-S reagent. (2) Checked against the standard prepared with A-C reagent. Average results only 0.0030 mg. per cc., less than the results of Group 1, which are easily within the experimental error. (3) Checked against the standard blue color reagent. Average results 0.0758 mg. per cc. more than the results of Group 1. (4) Checked against the standard blue color reagent. Average results 0.1485 mg. per cc. more than the results of Group 2. (5) Checked against the standard prepared with the E-S reagent. Averaged results 0.1368 mg. per cc. higher than the results of Group 1. (6) Checked against the standard prepared with the A-C reagent. Average results 0.0902 mg. per cc. less than the results of Group 1, and 0.2072 mg. per cc. less than the results of Group 5.

The assays were made in the manner shown in order to check and cross check the different reagents and to see whether it is possible to substitute one for the other. The results seem to check only when the unknown and the known are prepared with the same reagent, which should be the logical result.

The results obtained with the colorimetric method do not seem to justify the substitution of the A-C reagent for the E-S reagent. There is some possibility of the iron in the A-C reagent giving an additional color, which might interfere with the reading.

In comparing the results of Groups 1 and 2 with Groups 3 and 4, it is necessary to know whether the standard color dye solution was made up to correspond with the E-S reagent or with the A-C reagent. This laboratory has also been experimenting with various dye substances with a view to substituting a color standard for the alkaloidal standard.

We took the liberty of changing the directions slightly under the heading "Colorimetric Determinations." Instead of adding 1 cc. of water we used 1 cc. of the tartaric acid solution. As nearly all of the preparations was used in this colorimetric test we could not do anything with the biological test.

We also found that the extraction of the ergot alkaloids, whether from a solid or fluidextract, is made very successfully in the Watkins extraction apparatus, as suggested by Swanson [*J. Am. Pharm. Assoc.*, 229 (1932)]. Results 0.03 to 0.05 mg. per cc. higher were obtained by the extraction method in preference to the shake-out method; then too, emulsification is avoided in the extraction process, and many of the fluidextracts found in the commercial channels are not so clear as those prepared in the laboratory.

*W. J. Rice, Eli Lilly & Co., Indianapolis, Ind.*

*Results expressed in terms of ergotamine tartrate*

minutes	E-S REAGENT g./100 cc.	S-A-C REAGENT g./100 cc.
45	0.039	0.04
75	0.04	0.04
120	0.04	0.04
180	0.04	0.04

At the end of 3 hours a colorimetric comparison was made of a standard ergotamine tartrate solution, the color of which had been developed by the E-S reagent, and one in which the color was produced by the S-A-C reagent. The color did not match. The E-S reagent produced a blue-violet color, whereas the S-A-C reagent developed a lighter pure blue color. The unit scale readings were as follows:

$$\left. \begin{array}{l} \text{Ehrlich-Smith} \\ \text{Smith-Allport-Cocking} \end{array} \right\} = \frac{25}{20} \frac{20}{16}$$

The color of the standard solution of blue dye is the same quality of blue as that developed by the standard ergotamine tartrate solution and the S-A-C reagent, but it appears to be several shades lighter. Colorimeter readings on the two solutions are given as follows:

	45 min.		1 hr. 15 min.	
Standard Ergotamine Tart. + S-A-C Reagent	20	25	20	25
Standard Blue Dye Solution	25	30	25	30

(1) Whether the lighter color of the standard blue dye solution is due to fading or to a possible variation in technic on the part of different individuals we are unable to say. (2) We found that the results obtained on the submitted samples of fluidextract of ergot are the same regardless of the reagent used in developing the color. Yet our experience shows that the colors developed by the two reagents are not sufficiently alike to enable one to use the color standards interchangeably. (3) In making these determinations we used a Bausch & Lomb, Model 2502 Colorimeter, while the colors were developed in glass shell vials  $\frac{1}{2}$  inch in diameter and  $2\frac{1}{2}$  inches deep.

*James C. Munch and Amelia Ponce, Sharp & Dohme, Glenolden, Pa.*—Our studies indicate a good agreement between tests on the same product by the U.S.P. cock's comb and the Broom-Clark method; by the S-E reagent; and by the A-C reagent. However, the agreement between the bioassay and the chemical assay was not good. The A-C seems to offer certain advantages over the S-E: it is more rapid; it is not dependent upon weather conditions; and it gives equally good agreement against the standard used.

The artificial "standard blue dye" solution furnished proved suitable for use. We were unable to determine any alterations in color, so long as the solution was properly protected.

The method as modified says to "extract with ether, using 40, 25, 20, 15 cc. portions, or until the alkaloids are removed completely." These volumes of ether seem to be sufficient, but there is uncertainty about complete removal.

The method says to "shake the ether with an aqueous 1 per cent tartaric acid solution, using 10, 10, 10, and 5 cc. portions, respectively, or until alkaloids are removed completely," but how is one to know whether these four shake-outs completely remove the alkaloids.

The method also says to "evaporate the acid solution on a water bath in a current of air, etc." In one series of tests this procedure was varied: The combined ether solutions after washing were shaken with 1 per cent tartaric acid, 10, 10, 5, 5, 5, and 5 cc. being used. The tartaric acid solutions were combined, giving a volume of approximately 38 cc., which was made up to 40 cc., and 1 cc. was used for the colorimetric determination. The results are shown in the table.

The results observed in the colorimetric assays are presented in detail in the table. In addition to the A.O.A.C. fluidextract presented, tests were made upon a commercial sample of ergotole (an aqueous ergot preparation prepared to be essentially alkaloid-free), and a solution of ergotamine tartrate, which was stored in the refrigerator for 8 months.

Under the heading "Ehrlich-Smith reagent" the results are tabulated in terms of color values, interpreted as percentages of ergotamine tartrate; the color comparisons, when the color standard was developed by the E-S reagent, are given under the first sub-heading; when the color standard was developed by the A-C reagent, in the second column; and when comparisons were made with the artificial dye solution in the third column. Similarly results obtained when the unknown solution was treated with the A-C reagent are given in the last three columns, and the same remarks apply to the classifications for the color standards under that heading.

It would be expected that the color standard should be developed by the same reagent used for the development of the color of the unknown solution. However, it appeared of interest to compare the colors developed by the two reagents with the standards simultaneously developed by the two reagents, in order to learn whether there was any consistent difference in behavior. Inspection of the table shows clearly that more concordant results are obtained when the same reagent is used in both cases.

It appears that the results obtained by each reagent with the unknown and the standard agree within the limit of experimental error. When the unknown was treated with the Ehrlich reagent and the standard with the A-C reagent, slightly lower results were usually obtained, and the same general trend was observed when the A-C reagent was used for the unknown and for the standard.

While these assays are not to be considered as conclusive, there appears to be a slightly higher value when the unknown is treated with the A-C than with the E-S reagent, and comparisons are made with the artificial dye solution.

A few assays were made comparing ergotoxin ethanesulfonate with ergotamine tartrate solution. The colors developed appeared identical in hue, tint, and shade. The suitability of ergotoxin as a color standard is being further investigated.

PRODUCT	DATE OF ASSAY 1933	EHRlich-SMITH REAGENT COLOR STANDARD			ALLPORT-COCKING REAGENT COLOR STANDARD		
		E-S REAGENT	A-C REAGENT	DYE	E-S REAGENT	A-C REAGENT	DYE
		per cent	per cent	per cent	per cent	per cent	per cent
A.O.A.C.							
F. E. Ergot	9-7	0.046	0.048	0.056	0.045	0.046	0.053
	9-8	(0.050)	(0.043)	(0.060)	(0.056)	(0.050)	(0.068)
	9-22	0.057	0.050	0.068	0.060	0.054	0.070
Ergotole	9-22	0.0065	0.0063	0.0075	0.0079	0.0068	0.0094
0.1% Ergotamine tartrate soln. 8 mos. old	9-7	0.085	—	—	—	0.085	—

Clifford S. Leonard, *The Burroughs Wellcome & Co., Tuckahoe, N.Y.*—

Comparisons with Standard Ergotamine Solution	Volume of fluidextract per cent
Ehrlich-Smith reagent	0.0365
	0.0385
	Av. 0.0375
Allport-Cocking reagent	0.0375
	0.0400
	Av. 0.0387
B. W. & Co. H <sub>2</sub> O <sub>2</sub> method	0.0375
	0.0383
	Av. 0.0379
Comparison with Standard Color Solution	per cent
Ehrlich-Smith Reagent	0.038
Allport-Cocking Reagent	0.0410

The difference in color quality of standard and unknown made matching somewhat difficult. Our experience has been with pure solutions of ergot alkaloids rather than with Fl. Ext. Ergot.

Despite prompt and consistent refrigeration of the standard ergotamine solution after receipt, a fungus growth was noted. Some insoluble residue was noted in the standard dye solution. The color development was done in test tubes and transferred to the cups of micro Dubosque colorimeter.

We cannot consider that significant differences were to be seen in any of these tests. The rapid appearance of growth in the ergotamine standard solution would be indication for preparation of fresh standard from the crystalline alkaloid salt at frequent intervals.

#### H<sub>2</sub>O, AND H<sub>3</sub>PO<sub>4</sub> METHOD FOR COLORIMETRIC ASSAY OF ERGOT ALKALOIDS

The color development may be done in the dark in 10 minutes. The pure blue color has no red component and we believe it easier to match in the colorimeter. The correct strength of H<sub>2</sub>O<sub>2</sub> is important (0.1 cc. of "superoxal" Merck per 100 cc.); 0.1 cc. of this dilute H<sub>2</sub>O<sub>2</sub> is taken for the color development. The reagent is 1% of paradimethylaminobenzaldehyde dissolved in 40% H<sub>3</sub>PO<sub>4</sub>; H<sub>2</sub>SO<sub>4</sub> gives a purple color instead of the blue. The determination is carried out as follows:

A convenient quantity of the solution of ergot alkaloid (1 cc. of a 0.033% solution of ergotoxine ethanesulfonate gives a desirable color depth for colorimetric comparison) is treated with 10 cc. of concentrated H<sub>3</sub>PO<sub>4</sub>, 0.5 cc. of 1% reagent, and 0.1 cc. of dilute H<sub>2</sub>O<sub>2</sub>. After thorough mixing, the solution is allowed to stand for from 10 to 30 minutes and the color is compared to that of a standard similarly prepared.

#### DISCUSSION

The fluidextract was prepared in this laboratory in July from a lot of ergot recently received from Belgium. As it was not aged six months slightly more hydrochloric acid than specified by the U.S.P. was added to aid stability.

On August 12th, when it was sent to the collaborators, an assay with Smith-Allport-Cocking reagent showed 0.055 per cent. The results received before the middle of September from six collaborators were in fair agreement with the initial assay, but the results received later from two collaborators were 0.04 and 0.039 per cent, respectively. (Deterioration of the fluidextract or the standard solution of ergotamine tartrate was indicated.) On October 20th all solutions were re-assayed, and a newly prepared standard of ergotamine tartrate was used. A portion of the fluidextract stored at room temperature showed 0.030 per cent; the fluidextract stored in the refrigerator at 6°C. was 0.050 per cent. Incidentally the original stock solution of ergotamine tartrate, though containing mold, had not changed.

Because the fluidextract was unstable during the period of analyses, a tabulation for the purpose of comparing the extent of variation in the collaborative results is unwarranted. That the individual results were sufficiently accurate for the alkaloidal content at the time of analysis was confirmed by Leonard, who obtained 0.038 per cent by the ergotoxine-

phosphoric acid-hydrogen peroxide method and 0.039 per cent by the Smith-Allport-Cocking reagent. It was confirmed by Rice, who obtained low results by the cock's comb assay and colorimetric method. Five bioassays made by Munch and Ponce showed an average potency of 0.04 per cent by the Broom-Clark method, and bioassays by the cock's comb method showed a potency of 120 per cent of U.S.P. standard F. E. Ergot.

The comments of the collaborators contain many interesting contributions. Shupe states that the tartaric acid solution of extracted alkaloids showed no loss on evaporation to dryness and suggested a test for complete extraction of the alkaloids which insures quantitative accuracy. This step will be incorporated in the method.

Munch and Ponce pointed out that a commercial aqueous ergot extract prepared to be essentially alkaloid-free contained a small quantity of alkaloids when assayed by the colorimetric method.

It is believed that sufficient work has been done to show that the colorimetric method compares favorably with the biological assays. The time required for assay of the fluidextract is about 3 hours.

It is recommended<sup>1</sup> that study of the chemical assay of alkaloids of ergot be continued, with reference to standards, particularly those of ergotoxine ethanesulfonate.

No report on biological testing was given by the associate referee.

## REPORT ON NITRITES IN TABLETS

By FRANK C. SINTON (U. S. Food and Drug Administration,  
New York N. Y.), *Associate Referee*

The U. S. Pharmacopoeia recognizes a method of assay for sodium nitrite, also a method for the assay of spirit of ethyl nitrite. The former is a permanganate titration, while the latter is a gasometric determination. For the assay of nitrites in tablets, when no interfering material is present, it has been found possible to adapt one of these methods. The necessity for a study of this topic arose, however, when in the course of regulatory work tablets were encountered which contained organic matter, interfering with the permanganate method, and sodium bicarbonate, which made the gasometric method inapplicable. Therefore the work on this subject was confined to methods suitable for such a mixture.

A method that was considered less likely to be influenced by organic material and to be satisfactory in the presence of bicarbonates is one em-

<sup>1</sup> For report of Subcommittee B and action of the Association, see *This Journal*, 17, 53 (1934).

ploying potassium chlorate and silver nitrate reagents. For purposes of control a sample of "Sodium Nitrite C.P.," dried in a desiccator, was assayed by this method, also by the U.S.P. method, and the A.O.A.C. Devarda method for nitrates in salts. The results follow:

METHOD	per cent	SODIUM NITRITE per cent	per cent
1. Potassium chlorate	99.32	99.12	99.22
2. Modified U.S.P.	99.26	99.13	99.03
3. A.O.A.C. Devarda	99.12	98.35	99.05

No. 2 was reported as a modified method because it was found impossible to get a satisfactory end point titrating with oxalic acid, as directed in the U.S.P. On adding an excess of oxalic acid and titrating with permanganate the end point was satisfactory.

As the potassium chlorate method gave good results on the control, it was decided to try it out on a sample of tablets collected in the course of regulatory work. These tablets offered difficulty in the assay by the U.S.P. methods. The composition was as follows: sodium nitrite 1 gr.; sodium bicarbonate 2 grs.; F.E. Crataegus Ox., 1 min.; nitroglycerin 1/1000 gr.

The method follows:

#### REAGENTS

- (a) *Potassium chlorate solution*.—Saturated.
- (b) *Nitric acid*.—Concentrated.
- (c) *Silver nitrate solution*.—0.1 N.
- (d) *Potassium thiocyanate*.—0.5 N.

#### PROCEDURE

Count and weigh a representative number of tablets and powder at least 25, mixing thoroughly. Transfer to a 100 cc. volumetric flask a sample equivalent to about 0.5 gram of sodium nitrite, make up to volume with distilled water, shake thoroughly, and when solution has been assured, filter. Reject the first 10 cc. of solution, then transfer a 50 cc. aliquot to a 200 cc. volumetric flask. Add 5 cc. of nitric acid, 10 cc. of the potassium chlorate solution, and 20 cc. of the silver nitrate solution. Make up to volume with water, shake thoroughly, and when the silver chloride has settled, filter, rejecting the first 20 cc. Titrate a 100 cc. aliquot of the filtrate with the potassium thiocyanate solution.

1 cc. of  $\text{AgNO}_3$  0.1 N = 0.020703 gram of  $\text{NaNO}_2$ . Make determination of chloride if any is present in the tablet, and deduct from total.

#### RESULTS

$\text{NaNO}_2$  per average tablet: (1) 0.0593 gram; (2) 0.0597 gram U.S.P. sodium nitrite per average tablet (basis 95 per cent  $\text{NaNO}_2$ ): (1) 0.0624 gram; (2) 0.0628 gram.

These tablets were also run by the A.O.A.C. method for nitrates in salts (Devarda method). By this method  $\text{NaNO}_2$  per average tablet was

0.0590 gram, equal to 0.0621 gram U.S.P. sodium nitrite (95 per cent  $\text{NaNO}_2$ ).

These results indicate that the potassium chlorate method is satisfactory for the determination of nitrites. The method also appears satisfactory for the determination of nitrites in tablets having a composition similar to the one studied. It is recommended<sup>1</sup> that a collaborative study of the method be made.

## REPORT ON OINTMENTS

By WILLIAM F. REINDOLLAR (Department of Health,  
Baltimore, Md.), *Associate Referee*

The literature was investigated, and several methods were formulated and tried out.

Iodine ointment has been recognized under various formulas in the last six United States Pharmacopoeias, and it will again be official in U.S.P. XI. Although the quantity of iodine—4 per cent—has remained unchanged, the potassium iodide has been raised from 1 to 4 per cent (U.S.P. 1890), and the solvent has been changed from water to glycerin (U.S.P. 1900). The ointment base, which in 1870 was lard, was changed in 1880 to benzoinated lard, and in 1900 to wool fat. U.S.P. XI will carry the following formula:

	<i>grams</i>
Iodine	4
Potassium iodide	4
Glycerin	12
Wool fat	5
Yellow wax	5
Petrolatum	70
<hr/>	
To make	100

The iodine and potassium iodide are dissolved in the glycerin, and to this solution is gradually added and incorporated the previously mixed and liquefied fats.

In the earlier formulas the iodine combined rapidly with the fat and was present as the element only in traces. As the principal purpose of iodine ointment is to supply the therapeutic properties of iodine by inunction, this purpose was largely defeated by the nature of the ointment base. Hence the following changes were made: (a) from water to glycerin, because glycerin retards adsorption; (b) from a fat with a high iodine value to one with a comparatively low one, and finally to petrolatum.

<sup>1</sup> For report of Subcommittee B and action of the Association, see *This Journal*, 17, 53 (1934).

As U.S.P. XI will soon become official the investigational work was carried out on an ointment made by that formula. The studies included an assay for iodine, and one for potassium iodide. Two promising methods are presented. The former is a modification of the method of L. H. Fried; the latter was developed in this laboratory.

*Method I, Free Iodine.*—Into a tared glass-stoppered Erlenmeyer flask, weigh accurately about 5 grams of ointment and warm gently on a water-bath until fluid. Add 30 cc. of chloroform and shake until apparently dissolved. Then add 30 cc. of distilled water and titrate with 0.1 *N* sodium thiosulfate, using starch indicator, and continue the titration until the blue color disappears after vigorous shaking and does not return in 1 minute.

*Method II.*—Same as Method I except that 0.1 *N* potassium arsenite solution is used instead of 0.1 *N* sodium thiosulfate.

*Method I, Potassium Iodide.*—Accurately weigh about 5 grams of ointment into an Erlenmeyer flask of suitable size and attach to a distillation apparatus, using as a receiver a glass-stoppered Erlenmeyer flask containing 1 gram of potassium iodide in 30 cc. of distilled water, and 30 cc. of chloroform. Allow the end of the condenser tube to dip into this mixture. Make all connections air-tight. Add 150 cc. of 5% sulfuric acid and 5 grams of ferric alum to the distillation flask and heat over a direct flame, very slowly at first, until all the purple vapors of iodine have distilled over. If any iodine condenses in the tube, remove the flame and allow the liquid in the flask to suck up into the tube, whence it will dissolve the iodine. Wash out the condenser tube with 20 cc. of distilled water. Titrate the distillate with 0.1 *N* sodium thiosulfate. From the total iodine found, deduct the free iodine, and from the difference calculate potassium iodide.

*Method II, Potassium Iodide.*—Transfer the contents of the flask from the iodine determination to a separatory funnel and draw off the aqueous layer into a glass-stoppered Erlenmeyer flask. Wash the original flask and chloroform layer with successive portions of distilled water, 10, 5, 5, 5 cc., and add the washings to the aqueous layer. Boil gently until the volume has been reduced to about 15 cc. Add 5 cc. of chloroform and 60 cc. of concentrated hydrochloric acid and titrate with 0.05 *M* potassium iodate solution until, after vigorous shaking, the purple color of the iodine disappears from the chloroform layer and does not reappear in 5 minutes. From the total iodine found deduct the free iodine, and from the difference calculate potassium iodide.

## DISCUSSION

The first method is long and somewhat cumbersome. The quantitative distillation of iodine is rather difficult. However, the total iodine is presented for titration entirely freed from the other constituents of the ointment.

The second method determines both constituents on a single sample. This is advantageous in that it economizes on time and material, and disadvantageous in that any error in the first determination unduly influences the second one. It obviates the cumbersome distillation procedure, but it requires two different solutions for the titrations. The final reagent is specific for iodides.

The 0.1 *N* potassium arsenite solution contains about 22 grams of po-



tassium bicarbonate, as suggested by Gooch, for the neutralization of hydriodic acid.

The Associate Referee considers that sufficient work has not been done to warrant a definite statement regarding the relative merits of the methods presented. Furthermore, minor changes may be necessary to increase accuracy, or to facilitate operation. It is therefore recommended<sup>1</sup> that the Associate Referee investigate these methods further with the intention of submitting them later for collaborative study.

## REPORT ON ACETPHENETIDIN IN PRESENCE OF CAFFEINE AND ASPIRIN

By L. E. WARREN (U. S. Food and Drug Administration,  
Washington, D.C.), *Associate Referee*

Tablets containing acetphenetidin, caffeine, and aspirin are on the market. In 1909 this Association described a method for the separation of acetphenetidin from caffeine,<sup>2</sup> which was later tentatively adopted,<sup>3</sup> and in 1924 a method for the determination of acetylsalicylic acid in the presence of acetphenetidin and caffeine was adopted.<sup>4</sup> However, no method for the determination of acetphenetidin in the presence of acetylsalicylic acid and caffeine has been adopted; consequently this problem was assigned last year. In addition to the determination of acetphenetidin an attempt was made to determine each of the medicinal ingredients in such a tripartite mixture.

The tentative method of the Association for the determination of acetylsalicylic acid in such mixtures consists essentially in hydrolyzing the acetylsalicylic acid to salicylic acid in a reflux apparatus by the use of sulfuric acid, extracting the liberated salicylic acid and caffeine with chloroform, washing the chloroform with sodium carbonate solution, and converting the salicylic acid into its iodo compound with iodine. Both Harrison and Glycart<sup>5</sup> noted that the hydrolysis of acetphenetidin by this method was incomplete in the reflux apparatus, and they considered this to be due to the presence of chloroform. Probably the reason is that the reaction by which the acetphenetidin is hydrolyzed to phenetidin sulfate and acetic acid is reversible in the presence of acetic acid. Under the usual procedure the acetic acid is volatilized, but in the reflux apparatus it is retained, and complete hydrolysis is prevented.

A mixture was prepared to contain:

<sup>1</sup> For report of Subcommittee B and action of the Association, see *This Journal*, 17, 53 (1934).

<sup>2</sup> U. S. Dept. Agr. Bur. Chem. Bull. 132, 198 (1909).

<sup>3</sup> *This Journal*, 2, 49 (1916).

<sup>4</sup> *Ibid.*, 8, 265 (1925).

<sup>5</sup> *Ibid.*, 8, 28 (1924).



	<i>per cent</i>
Acetphenetidin (phenacetin).....	33.33
Acetylsalicylic acid (aspirin).....	33.33
Caffeine citrate.....	1.67
Starch.....	31.67

Another mixture consisted of powdered tablets, the exact composition of which was unknown to the Associate Referee. Each tablet was stated to contain  $2\frac{1}{2}$  grains each of acetphenetidin and acetylsalicylic acid with  $\frac{1}{4}$  grain of caffeine citrate.

These mixtures and a suggested method of separation were sent to three collaborators.

The recoveries ranged, for acetphenetidin, from 95 to 104.7 per cent; for acetylsalicylic acid from 55.8 to 105.9 per cent; and for caffeine from 89 to 230 per cent.

In view of the small amount of collaborative work done and the variable results obtained it is recommended<sup>1</sup> that the topic be continued for another year.

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No report on strychnine in tablets was given by the associate referee.

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No report on pyridium was given by the associate referee.

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## REPORT ON GUMS

By J. H. CANNON (U. S. Food and Drug Administration,  
Chicago, Ill.), *Associate Referee*

A referee on gums in foods was appointed in 1931. Before the work on gums in drugs was begun this year, it was learned by correspondence that the study of the Referee on Gums in Foods has been confined to the locust bean in ice cream and cream cheese. These substances are also of importance in connection with drug preparations, not as adulterants, but because they are extensively used as medicinal agents, emulsifiers, and binders.

Gums, a word taken from the Greek and derived from the Egyptian "Kami"<sup>2</sup> is, according to the Encyclopedia Britannica, the generic name given to a class of uncrystallizable substances composed of carbon, hydrogen and oxygen that occur widely in plants, and to a limited extent in animals. Their chief characteristic is that they form viscous solutions or

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<sup>1</sup> For report of Subcommittee B and action of the Association, see *This Journal*, 17, 53 (1934).

<sup>2</sup> Real-Enzyklopadie Der Gesamten Pharmasie, 1905, vol. VI, p. 87.

mucilages either by dissolving in water (soluble gums) or by absorbing many times their own volume of that solvent (insoluble gums). Quoting from this authority, "Commercial gums contain more or less mineral matter, chiefly calcium, magnesium and potassium. A little nitrogen is also often present; but it is not an essential constituent. In this the gums differ from the gelatins, glues and proteins, which form solutions of a similar character; but which are definitely nitrogenous bodies." They are distinguished from resins and gum resins (to which the term gum is loosely applied,<sup>1</sup> e.g., gum benzoin and gum myrrh), by their total insolubility in alcohol.

Until the researches of O'Sullivan, published in 1884-1901, the chemistry of the gums remained obscure, doubtless because their uncrystallizable character made purification difficult and uncertain.<sup>2</sup> O'Sullivan showed that the principal substance in acacia consists of a complex acid combined chemically with certain sugars. It has been shown recently that the pectins have a similar composition.

Gums may be classified according to their content of arabin, cerasin, or bassorin,<sup>3</sup> the three principal gum substances. However, a method of identification based on hydrolysis products is too time-consuming to be of practical value in routine work. According to Jacobs and Jaffe,<sup>4</sup> who have reviewed the literature, the few available methods for the separation of gums from drugs do not lend themselves to use for identification purposes.

In 1929, Weinberger and Jacobs<sup>5</sup> published a method for the identification of gums by means of characteristic alcohol precipitates. This method is in itself insufficient to identify some of them positively.

In April 1931, Jacobs and Jaffe<sup>6</sup> published a method for the identification of the common gums by means of various inorganic and organic reagents which yield characteristic precipitates when added to dilute aqueous solutions. This method, with slight modifications, served as the basis for work done this year.

There were submitted to the collaborators directions for identification, control specimens of powdered gums, and unlabeled samples consisting of 0.2 per cent solutions of the gums in 5 per cent alcohol. Solution 1 contained quince seed; 2, Irish moss; 3, acacia; 4, karaya; 5, tragacanth; and 6, agar.

The collaborators were H. R. Bond, Geo. M. Johnson, and I. S. Shupe, U. S. Food & Drug Adm., Chicago; Harry J. Fisher and C. E. Shepard, Connecticut Agr. Exp. Sta., New Haven; L. E. Warren and C. D. Wright, U. S. Food & Drug Adm., Washington; W. L. Scovill, State Dept. of Agr., Lansing, Mich.

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<sup>1</sup> Webster's Dictionary.

<sup>2</sup> Encyclopedia Britannica (article on gums).

<sup>3</sup> Wiesner, *Die Rohstoffe des Pflanzenreiches*, vol. I, p. 82.

<sup>4</sup> *Ind. Eng. Chem. Anal. Ed.*, 3, 210 (1931).

<sup>5</sup> *J. Am. Pharm. Assoc.*, 18, 34 (1929).

<sup>6</sup> *Loc. cit.*

## METHOD FOR IDENTIFICATION OF SOME COMMON GUMS

## REAGENTS

- (a) *Ammonium molybdate*.—*Methods of Analysis*, A.O.A.C., 1930, 14.  
 (b) *Potassium hydroxide solution*.—10%.  
 (c) *Millon's reagent*.—*Methods of Analysis*, A.O.A.C., 1930, 650.  
 (d) *Neutral ferric chloride solution*.—10%.

## PREPARATION OF SAMPLES

*Control*.—Suspend 0.2 gram of the powdered gum in 5 cc. of 95% alcohol and pour into 95 cc. of cold H<sub>2</sub>O. Shake until no further solution is observed.

*Solid*.—Same as for control.

*Liquid*.—Evaporate to dryness, weigh residue, and prepare 0.2% solution.

## IDENTIFICATION

To 5 cc. of a 0.2% solution of the gum in a medium sized test tube add reagents in the order indicated in the following outline of tests:

GUM	REAGENT	TEST
Quince seed	Ammonium Molybdate	Opaque, gelatinous precipitate on heating after addition of 4 drops of reagent. (Other gums negative.)
Tragacanth	10% KOH	Deep yellow color on boiling after addition of 4 drops of reagent. (Acacia, faint yellow tinge, others negative.)
Karaya	Millon's reagent	White precipitate settles on standing 4–5 minutes after addition of 1 drop of reagent. (Other precipitates do not settle rapidly.)
Irish moss	10% FeCl <sub>3</sub>	Light colored opaque precipitate forms immediately on addition of 0.5 cc. of reagent. (Quince seed yields flocculent precipitate.)
Agar	10% FeCl <sub>3</sub>	Brown flocculent precipitate on heating after addition of 0.5 cc. of reagent. (Karaya yields similar precipitate.)
Acacia	10% FeCl <sub>3</sub>	Fine white precipitate forms slowly on addition of 1 drop of reagent. (No precipitate formed when an excess was added immediately as in test for Irish moss.)

## COMMENTS BY COLLABORATORS

*H. R. Bond*.—Identification of individual solutions well defined.

*H. J. Fisher*.—It seems to me that only the test for quince seed gum with ammonium molybdate and the test for Irish moss with ferric chloride in the cold are satisfactory, particularly when more than one gum is present in an unknown.

*Geo. M. Johnson*.—For simple identification of gums, the method seems to be fairly satisfactory.

*W. L. Scovill.*—In the description of Reagent (d) it is suggested that the word "neutral" be omitted, as in most of our food work neutral ferric chloride is usually taken to mean ferric chloride which has been partially neutralized with ammonium hydroxide. The partially neutralized  $\text{FeCl}_3$  is apparently not satisfactory for these tests.

*I. S. Shupe.*—The method given was considered satisfactory for the identification of the six gums mentioned. Observation of the action of the control is desirable especially with Millon's reagent.

*C. D. Wright.*—The method has been tried out with what appear to be satisfactory results.

#### DISCUSSION OF RESULTS AND COMMENTS

Five of the eight collaborators identified all gums correctly. The remaining three missed two gums each. To these were sent additional samples of the same solutions for check tests. The additional samples were correctly identified by two of the three, and no report was received from the third. This shows that the tests, with the possible exception of agar, are reasonably dependable, and for present purposes they are considered adequate.

Fisher evaporated the solutions, weighed the residues, made new 0.2 per cent solutions, and filtered before testing. Filtering was not specified in the directions.

Regarding the two suggestions of Scovill and Shupe, the Associate Referee is in agreement as further observations have shown them to be justifiable. Therefore, the method is amended as follows: Instead of "neutral ferric chloride solution—10 per cent," the directions shall read "Ferric chloride solution.—Dissolve 9 grams of ferric chloride in sufficient distilled water to make 100 cc.," and the words, "For every test use a blank or control in order to distinguish any change in the test solution due to the addition of the reagent," shall immediately follow the outline of tests.

#### RECOMMENDATIONS<sup>1</sup>

It is recommended—

(1) That the method submitted, exclusive of the test for agar, be adopted as tentative.

(2) That the test for agar be further studied.

(3) That further study of gums include suitable methods for their separation from drug mixtures.

#### REPORT ON ESSENTIAL OILS

By E. L. ANDERSON (U. S. Food and Drug Administration,  
New York, N.Y.), *Associate Referee*

Although considerable work has been done by this Association on the subject of essential oils most of it has been in connection with the oils con-

<sup>1</sup> For report of Subcommittee B and action of the Association, see *This Journal*, 17, 53 (1934).

tained in flavoring extracts and spices. There are also some methods of assays of essential oils in the United States Pharmacopoeia. Owing to the difficulty experienced with some of these U.S.P. methods in the course of regulatory work, it was decided to choose for this year's study an investigation of the determination of citral in lemon oil.

The present U.S.P. method may be satisfactory after considerable experience, but it gives trouble to the ordinary analyst in determining the end point. Because of this and also because of many current favorable comments on the British Pharmacopoeia method, a comparison of the two was undertaken. Sufficient work has not been done to warrant a definite conclusion, but indications point to a preference for the B.P. method in regard to time consumed, shortening of end point, and general workability. Results, however, are somewhat lower by the B.P. method than by the U.S.P. method.

It is recommended<sup>1</sup> that further study of this subject be made.

The Associate Referee on Resins and Oleoresins reported that he had sent two samples of podophyllum to collaborators to be assayed for resin by a method suggested, that no reports were received, and that he recommended that the subject be continued.

The paper, entitled "Some Observations on the Use of Automatic Extractors," presented by L. E. Warren, is published in *This Journal*, page 516.

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<sup>1</sup> For report of Subcommittee B and action of the Association, see *This Journal*, 17, 53 (1934).

## WEDNESDAY—MORNING SESSION

### SYMPOSIUM ON NEW ANALYTICAL METHODS

At the symposium on analytical methods held Wednesday morning the following papers were presented. References are given for those that have been published.

1. An Apparatus for the Study of Reactions under Mechanical Pressure, by Kenneth C. Beeson and John B. Kershaw, *This Journal*, 17, 320 (1934).

2. Study of Accuracy of the Kjeldahl Method. III. A Further Comparison of Selenium and Mercury Catalysts, by R. A. Osborn and A. Krasnitz, *This Journal*, 17, 339 (1934).

3. Colorimetric Method for Small Quantities of Rotenone, by C. M. Smith and C. R. Gross, *This Journal*, 17, 336 (1934).

4. Further Study of Arsenic in Plant Material, by J. A. Schricker (to be published later).

5. Selenium, by W. O. Robinson, M. J. Horn, and J. Davidson. Part of this material was published in the following papers: Qualitative Method for Selenium in Organic Compounds, by M. J. Horn, *Ind. Eng. Chem. Anal. Ed.*, 6, 34 (1934), and Determination of Selenium and Arsenic by Distillation, by W. O. Robinson, H. G. Dudley, Kenneth T. Williams and Horace G. Byers, *Ind. Eng. Chem. Anal.*, 6, 274 (1934).

6. Lead, by H. J. Wichmann, F. A. Vorhes, Jr., and P. A. Clifford. This paper was published by H. J. Wichmann, C. W. Murray, M. Harris, P. A. Clifford, J. H. Loughrey and F. A. Vorhes, Jr., under the title, Methods for Determination of Lead, *This Journal*, 17, 108 (1934).

7. Milk in Milk Bread, by V. E. Munsey.

8. Importance of Enzyme Analysis in Agricultural Chemistry, by A. K. Balls (see p. 531).

9. Salad Dressing in General and French Dressing in Particular, by C. H. La Wall and Joseph W. E. Harrison.

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### CORRECTION

For cut on p. 72, Vol. 17, No. 1, *This Journal*, substitute the cut shown on p. 372 of this number.

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### IMPORTANT NOTICE

The November number of *The Journal* will be devoted to an index of the proceedings of the Association from its organization in 1884 to 1930. In addition a booklet in commemoration of the 50th Anniversary of the Association will be issued.

As the proceedings for 1933 are completed in this number, the annual index also appears here instead of in its usual place in the November number of *The Journal*.



## CONTRIBUTED PAPERS

### MARYLAND'S EARLY FERTILIZER LAWS AND HER FIRST STATE AGRICULTURAL CHEMIST\*

By F. P. VEITCH (U.S. Bureau of Chemistry and Soils,  
Washington, D.C.)

Very little information on the history of the early fertilizer legislation and on the early state agricultural chemists of the country seems to be readily available.

It was long my understanding that either Connecticut or Massachusetts was the first to pass a State fertilizer law. Ross, in the chapter "The Chemist and Policeman on Fertilizer, Feed, and Insecticide Control," in "Chemistry in Agriculture" (1926), while not specific on the point, states (p. 365): ". . . the first laws enacted in each State (Connecticut and Massachusetts) in the year 1869 were ineffective, no definite provision being made to carry out the requirements of the laws." Also, "On May 26, 1873, a law was enacted by the Massachusetts Legislature which provided for the official inspection and analysis of fertilizers in the State, it being required that all fertilizers offered for sale have a guarantee of composition attached." Ross also says (p. 366), "It is believed that this is the first effective fertilizer-inspection law enacted in the United States, although fertilizer-inspection laws were enacted both in Alabama and Delaware in 1871, the provisions of the Alabama law, however, being unworkable and the operation of the law being abandoned." The inference is, therefore, that fertilizer laws were first enacted either in Connecticut or in Massachusetts.

However, it is not my purpose to decide which state first enacted fertilizer inspection laws; I am presenting now the record so far as I have it of such legislation in Maryland. I may add, however, that Massachusetts had a lime inspection law as early as 1785, that Virginia had a lime and guano inspection law as early as 1852, and Pennsylvania as early as 1860. Both were probably enacted the year before these dates.

In studying the early development of scientific agriculture in this country, I came across records showing the enactment of a plaster Paris inspection law (Chap. 282), and a lime inspection law (Chap. 269) in Maryland in March, 1833, and the enactment of a law establishing the position of State Agricultural Chemist in March, 1848 (Chap. 249), followed by amendments to these inspection laws in 1847, 1848, 1854, 1868, 1870, 1886, 1890 and later.

In considering fertilizer-inspection laws, we must, of course, bear in

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\* Presented at the Annual Meeting of the Association of Official Agricultural Chemists, November, 1932

mind the situation at the time such laws were enacted. In 1833 the word "fertilizer" was rarely used, although the word itself dates back to 1661.

Farm manures, industrial wastes, stamped raw bones, gypsum or land plaster, and Peruvian guano brought to the attention of the world in 1804 by Humbolt were the fertilizers known to the farmers of that day; they were designated by the general term "manures" or by a specific term for each material. Apparently Peruvian guano was first imported into this country in 1824 (Wheeler). The importation consisted of two barrels and was made by John S. Skinner of Prince Georges County, Maryland, who stood in the front rank of progressive planters of his day and was the founder in 1819 of *The American Farmer*. The importation, according to this journal, entered through the port of Baltimore, Maryland.

These then were the fertilizers of that day. Contradictory results in different sections of the state and even on contiguous farms with gypsum, or, as it was commonly called, plaster Paris, led to the passage in March, 1833, of an act from which a few excerpts are given for their possible historic interest.

Chapter 282.—An Act to provide for the Inspection of Plaster Paris, in the City of Baltimore.

WHEREAS, It is of importance that Plaster Paris should be of good quality, accurately weighed, and well coopered;

Therefore,

Sec. 1. Be it enacted by the General Assembly of Maryland, That the Governor, . . . shall appoint a person of integrity and good character, as Inspector of Plaster Paris, in the city of Baltimore.

Sec. 2. Oath.

Sec. 3. . . . That it shall be the duty of said Inspector, whenever required to do so, to inspect all Plaster, in lump or stone, that shall be brought to the city of Baltimore.

Sec. 4. Inspector shall weigh.

Sec. 6. . . . That if any person or persons in the city of Baltimore, shall sell, or offer for sale, any Plaster Paris, unless the same shall have been inspected, he or they shall forfeit and pay for each and every offence the sum of five dollars, for each and every ton so sold or offered for sale, . . . .

On March 15, 1834, in Chap. 275, the Legislature amended this Act imposing a penalty of \$20.00 for each violation and reducing the Inspector's fee to 6 cents for each 320 pounds net weight. The 3rd, 4th, 5th and 6th sections of the act of March 22, 1833, were repealed.

At the next session of the Legislature and early in 1834 essentially the same law (Chap. 20) was passed for the port of Bladensburg, Maryland, the Levy Court of Prince Georges County being given the power to appoint annually an Inspector of Plaster Paris.

It will be noted that these laws were public local law for Baltimore and Bladensburg only, and not public general laws, the reason being that Baltimore and Bladensburg were the only ports in the state where plaster

Paris could be bought in quantity. It will also be noted that no provision is made for analysis, the inspection apparently consisting simply of weighing the barrels of plaster, which were required to be well coopered and to contain not less than 320 pounds of plaster net. From this fact we may reasonably assume that there was little or no sophistication and little knowledge of the valuable components of plaster. The lime inspection law (Chap. 269) passed early in 1833 was similar, the requirement being that the lime should be measured, and standards were established for quality in Sec. 8, which reads that "All lime that is clean of core, gravel, sand, and dirt, shall be considered first quality, and so on in proportion with other lime less fine, according to the judgment of the inspector, until it is reduced to third quality or condemned as hereinbefore mentioned."

These laws, although they appear to have been observed and useful to a limited degree, of course fell far short of being satisfactory. Later, however, the importation of Peruvian and other guanos into Maryland through the port of Baltimore became quite extensive, and the variable crop results obtained with them led, after much agitation in the agricultural journals, to the passage, March 10, 1847, of the following Act (Chap. 341), which is also quoted in part:

Chapter 341.—An Act to provide for the Inspection of Guano in the City of Baltimore.

Sec. 1. Be it enacted by the General Assembly of Maryland, That the Governor, with the advice and consent of the State, shall, . . . appoint a practical chemist of integrity and good character, as inspector of Guano in the city of Baltimore.

Sec. 3. . . . That . . . , it shall not be lawful to sell, expose or offer for sale, any guano within the limits of the city of Baltimore, . . . unless the same shall have been first inspected and marked or branded by the inspector appointed by virtue of this act, under the penalty of twenty dollars for each and every violation of this act. . . .

Sec. 4. . . . That it shall be the duty of the inspector appointed by virtue of this act to inspect analytically all guano which may hereafter be exposed or offered for sale, or sold, within the limits of the city of Baltimore, . . . and to put proper marks on the same, denoting the place of inspection, and the quality and weight of guano contained in each bag, barrel, keg or cask of any kind, making the proper allowance for the weight of the bag, barrel, keg or cask of any kind in which said guano may be contained, according to the best of his judgment.

Sec. 6. . . . That from any judgment rendered by any justice of the peace, in pursuance of this act, either party to such judgment may appeal to Baltimore county court, in the same manner, and under the same regulations as is allowed from judgments rendered by justices of the peace in cases of small debts.

It will be noted that this law provided that all guano imported through Baltimore should be inspected "analytically," and that the inspector, who should be a practical chemist of integrity and good character, should place on the containers the proper marks denoting the place of inspection and the quality and weight of guano contained in each container. The act imposed a penalty of \$20.00 for each violation of it.

On March 10, 1848, the Maryland legislature passed an act (Chap. 317) supplementing the act relating to the inspection of plaster Paris and guano in the City of Baltimore, extending the provisions of Sec. 3 of the original acts to the limits of the State of Maryland and requiring "That the inspector of Plaster Paris shall, from and after the passage of this act, determine the quality thereof analytically."

I have found no data on which to determine how strictly this law was enforced, but the evidence is that it proved far from satisfactory, and there is much interesting and amusing matter in *The American Farmer* during the next five or six years about the inadequacy of the fertilizer laws. Indeed, the State Agricultural Chemist, appointed by the Governor in May, 1848, made it one of his most cherished duties to go after the plaster and guano inspections hammer and tongs during the early years of his incumbency and was finally largely instrumental in having passed an amendment to the Act of 1847. This amendment (Chap. 317) was passed March 10, 1854, and reads in part as follows:

Chapter 317.—WHEREAS, the inspection of all articles should show as nearly as possible the quality of the article inspected; And whereas, the chief valuable constituents of guano, are its ammonia and phosphates; Therefore,

Sec. 1. Be it enacted by the General Assembly of Maryland, That . . . , all guano landed, transhipped, sold or offered for sale in the State of Maryland, shall be analyzed so as to show the percentage of its ammoniacal and phosphatic compound, and that the quality thus ascertained shall be marked upon each bag, barrel, cask, tierce, box, package or parcel, or upon anything containing the guano, in accordance with the following scale, commencing with the latter A. which shall indicate in Peruvian Guano, that the parcel so marked contains from fifteen to eighteen per cent, of Ammonia, the letter B. indicating from twelve and a half to fifteen per cent, the letter C. indicating from ten to twelve and a half per cent, the letter D. indicating from seven to ten per cent. A similar table shall be arranged by the inspector to indicate the quantity of phosphates contained in Mexican and Patagonian Guano, and upon other variety of guano, similar marks indicating its quality shall be used.

Sec. 2. . . . That the inspector of guano shall for the information of the public cause these tables to be published, and shall also publish in the agricultural journals of the State, and in one or two daily papers in Baltimore city, the analysis of samples of each and every cargo with the name of the vessel in which the same was imported.

Sec. 3. . . . That the inspector shall keep an office in some convenient part of the city of Baltimore, and shall keep an analysis of every cargo or parcel of guano inspected by him, and shall enter or have the same entered in a book to be kept for that purpose, and shall by himself or some other person having charge of his books give to any person desirous of purchasing guano, a copy of the analysis of such cargo, or parcel then in market for sale.

Sec. 5. Imposed fines for not having guano inspected.

Sec. 6. Prohibited sale of uninspected guano.

This act required the State Inspector to place marks on the containers indicating the grade of the guano as determined by its content of ammonia and phosphates, required the publication of the analyses of each cargo, including the name of the vessel on which imported in the agricul-

tural journals of the state and in the Baltimore city papers, and required the inspector to have an office in Baltimore where the results of analyses of each cargo should be kept and where information concerning any cargo of guano was to be given to any person seeking it.

On the same date, March 10, 1854, the plaster Paris law, passed in 1833 and as subsequently amended, was repealed, and the state chemist was required to analyze samples for any person going to sell or buy plaster Paris and to give him a certificate showing the properties of the sample, all for the price of 50 cents per sample.

About this time (1845-1855), commercial or "manipulated" fertilizers, as they were called, began coming on the Maryland market in quantity. At first these were chiefly dissolved animal bone, but were shortly followed by mixtures of various fertilizer materials. Consequently the need for additional laws was felt since it would appear that legally the guano laws did not cover manufactured fertilizers, and on March 30, 1868, the legislature passed an amendment (Chapter 295) relating to the inspection of all fertilizers other than guano. The more important parts of this act read as follows:

Chapter 295.—Sec. 1. Be it enacted by the General Assembly of Maryland, That an Inspector shall be appointed, whose duty it shall be, on oath, to inspect all fertilizers other than guanos, imported into and manufactured in the State of Maryland, and to show by chemical analysis the percentage of valuable constituents in said fertilizers, and to mark same upon all bags, packages, or on whatever may contain the same, used, sold or offered for sale, with the receipt therein; and when the same shall be inspected in bulk, then the Inspector shall give a certificate in writing to the owners or consignees of said fertilizers, or their agents, of the analysis of said fertilizers, so as to show its percentage of valuable constituents in phosphate of lime, in ammonia, which already may be formed in it, together with that capable of being formed from its nitrogenous compounds, copies of which shall be published in at least two of the daily papers in the city of Baltimore.

Sec. 2. . . . That it shall be the duty of said Inspector to analyze and examine all of the artificial, manufactured or manipulated manures which may be manufactured or sold in the State of Maryland, so as to show the consumer the value of such manures, and publish the same once in every week in two of the daily papers of the city of Baltimore.

Sec. 3. . . . That the said Inspector shall keep an office in the city of Baltimore, and in it a record of all the examinations of manures of all kinds made by him, which at all reasonable times shall be shown to those who may wish to examine the same.

Sec. 4. Penalties for not having packages inspected.

Sec. 5. Penalties for not having inspected when in bulk.

Sec. 6. Use of previously used containers bearing inspection marks prohibited.

Sec. 7. . . .

Sec. 8. . . . That the said Inspector shall be a practical analytical and agricultural chemist of good repute, and shall hold his office for two years, and until his successor is appointed; the said Inspector shall be appointed by the Superintendent of Labor and Agriculture. . . .

William McPherson, Superintendent of the Department of Labor and

Agriculture of Maryland, in his report for 1868 and 1869 states that this law was rendered inoperative by the omission of an important section, the rate of fees for the inspection. He suggests that the inspection laws should require the inspection of all fertilizers brought into the state as well as those made there, that the inspection of guano and of commercial fertilizers could be advantageously entrusted to one officer, and that much of the work might be conveniently and profitably committed to the chemical laboratory of any of the institutions of science and learning fostered by the state.

On April 4, 1870, the legislature repealed the Act of 1868 and added an additional section to the code of public general laws (Chap. 426). The more important parts read:

Chapter 426.—Sec. 1. Be it enacted by the General Assembly of Maryland, That the Act entitled an Act to amend Article four of the Code of Public Local Laws, title Guano, by adding thereto the following Sections relating to the inspection of all fertilizers other than Guano, passed at January session, eighteen hundred and sixty-eight, Chapter two hundred and ninety-five, be and the same is hereby repealed, and an additional Article is hereby enacted and added to the Code of Public General Laws to number one hundred and thirteen, and titled "Manures and Fertilizers," to read as follows: All commercial manures and artificially manufactured or manipulated fertilizers, brought into or manufactured in the State of Maryland for sale and sold or kept for sale therein, shall have permanently affixed to every sack, bag, barrel, box or other package thereof a stamped or printed label, which shall specify legibly the name or names of the manufacturer or manufacturers, his, her or their place of business, the net weight of each sack, bag, barrel, box or other package, the components parts of such manure or fertilizer, the percentage by weight, which it contains, of the following constituents, viz., of phosphoric acid soluble in pure cold water, of phosphoric acid insoluble in pure cold water, of available ammonia, potash and soda. That if any person shall sell or keep for sale any commercial manures, or artificially manufactured, or manipulated fertilizers not labeled in accordance with the requirements of the next preceding Section or shall affix any label to any sack, bag, barrel, box or other package, not expressing truly the component parts of said manures or fertilizers, or expressing a larger percentage of the constituents or either of them mentioned in the next preceding section, than is contained therein, shall be punished by a fine of fifty dollars for the first offence and seventy-five dollars for the second, and each subsequent offence, to be recovered on indictment and conviction in the Circuit Court of Baltimore City or the Circuit Court for the County, within whose jurisdiction said offence may be committed, one-half thereof to be paid to the informer, the other half to the State.

That any purchaser of commercial manures or artificially manufactured or manipulated fertilizers, bearing labels as provided for in Section one of this Article, who shall be injured or defrauded by the contents of the sacks, bags, barrels, boxes or other package not conforming in quality and quantity to the labels thereon, may recover from the seller or sellers thereof, in an action of debt, an amount equal to the purchase money of such manure or fertilizer. . . .

4. That the words "commercial manures, artificially manufactured or manipulated fertilizers," shall be taken and construed to include all manures and fertilizers which shall be sold for a greater price than one cent per pound. . . .

5. That by the term soluble phosphoric acid, whenever used in this Act, is meant phosphoric acid in any form or combination readily soluble in pure cold water, and

by the term insoluble phosphoric acid is meant phosphoric acid in any form or combination which requires the action of an acid upon it to cause to become readily soluble in pure cold water.

6. Prohibits adulterations and provides fines for adulterating.

The enforcement of all the foregoing acts was in the hands of inspectors designated for the purpose. The inspector was required to mark the results of his analysis on the containers and to make them public in the Baltimore papers and the state agricultural journals. No other type of publication seems to have been contemplated. The inspector was directly paid the fees provided in the act. Approved April 7, 1886. An act (Chap. 477) to regulate the inspection and sale of commercial fertilizers in the State of Maryland was passed, which imposed a license fee, made it the duty of the Maryland Agricultural College to analyze all samples sent to it for the purpose by any farmer, and gave the college the license fees provided they did not exceed \$2,000 per year. It imposed penalties for violation of the act by manufacturers, but made no provision for the taking of samples and their analysis independently by the college or for publication by the college of the results of analysis.

On April 3, 1890, further amendments to the state fertilizer laws were approved. The term fertilizer was more carefully defined, statement of chemical analysis on containers was required, the Agricultural College was required on its own initiative to take samples each year of fertilizers and to publish results of analysis of such samples from time to time. It provided for recovery of damages for injury or fraud from use of a fertilizer and prohibited adulteration.

Other amendments have followed from time to time, but are of no immediate interest in connection with this historical statement. I think though that I have given enough data to show that very early in the last century the matter of fertilizer composition and fertilizer inspection and analysis was receiving the attention of the progressive Maryland farmers and that legislation was early enacted with regard to the matter.

As I have said before, I am not at all sure that the laws above referred to are the first passed in this country. From the action of an agricultural convention held in Richmond, Virginia, (*Am. Farmer*, April 1, 1852), asking for the repeal of the inspection laws of guano, plastic and lime, it is quite clear that Virginia also had laws relating to these materials, and from another reference in the issue of November, 1860, that Pennsylvania had such laws that were entirely inadequate. I have not undertaken to search for these, and I am leaving to others the work and pleasure of doing so.

In this connection it occurs to me to suggest that it might be well worth while for members of this Association representing the agricultural chemists of the States organized before 1860, at least, to each prepare a paper which might well be read before this Association showing when the

first fertilizer laws of his respective State were enacted, telling also who was the first chemist in each instance and the general effect of the laws in question. I expect a number of such laws passed before 1860 will be brought to light.

#### THE STATE AGRICULTURAL CHEMIST

Thus we see Maryland passed her first fertilizer inspection law nearly 100 years ago, and might well celebrate its hundredth anniversary in 1933.

But what about the first State agricultural chemist? On March 9, 1848, the Maryland legislature passed an act entitled "An Act to Provide for the Appointment of an Agricultural Chemist for the State," (Chap. 249), which reads as follows:

Chapter 249.—An act entitled, an act to provide for the appointment of an Agricultural Chemist for the State.

Sec. 1. Be it enacted by the General Assembly of Maryland, That the Governor, by and with the advice and consent of the Senate, shall hereafter annually appoint and commission a person of ability, integrity and suitable practical and scientific attainments as Agricultural Chemist for the State, and if the Senate shall have adjourned before the Governor shall make the appointment for the present year, or if a vacancy shall hereafter occur during the recess of the Senate, then the Governor alone shall make such appointment, which shall be good, and valid until the tenth day after the next meeting of the Senate.

Sec. 2. . . . That the State shall be divided into three districts, the first shall comprise that part of the State now comprised in the first gubernatorial district, the second that of the third gubernatorial district and the third that of the second gubernatorial district.

Sec. 3. . . . That the said Agricultural Chemist shall spend one year, the first beginning on the date of his appointment, in each of said districts in the order named, it shall also be his duty to spend one month in each county and Howard district, and visit each election district.

Sec. 4. . . . That it shall be the duty of said Agricultural Chemist to analyze specimens of each variety of soil of the county in which he shall be that may be brought to him or that he may find to exist, and also to examine, and if necessary, analyze specimens of each kind of marl or other mineral or vegetable deposit that may come to his knowledge, in order that his instructions may be of more practical utility.

Sec. 5. . . . That it shall also be his further duty to deliver one public lecture, after having given timely notice thereof, in each election district in each county, and then to deliver a course of public lectures at each county town, and some central place in Baltimore county, after having given also sufficient notice thereof in each election district, and he shall also permit the clerk of the levy court, or of the commissioners of the tax, as the case may be, to take a copy of said course of lectures to be retained and kept for the use and benefit of the county, and published by said levy court or commissioners of the tax, if to them it shall seem expedient.

Sec. 6. . . . That the said Chemist shall make an annual report to the House of Delegates, if in session, and if not, then to the Governor, whose duty it shall be to cause the same to be published, of his proceedings and such other matters touching the Agricultural interest of the State as may be considered necessary.

Sec. 7. . . . That for the faithful discharge of his duties the said Chemist shall receive the annual salary of fifteen hundred dollars, to be paid as the salaries of



other civil officers are or may be paid, and for the purchase of chemical implements and materials the said Chemist shall be allowed for the first year the sum of two hundred dollars in advance, and on each succeeding year a sum not exceeding fifty dollars, out of such monies as may be in the treasury and not otherwise appropriated.

The act was amended in 1852 or 1853 (Chap. 195).

The amendment provided for the employment of an assistant chemist and located the permanent laboratory in the city of Baltimore.

So far as I have found, this is the first provision for a *State* agricultural chemist in this country, and this conclusion is strengthened by a paragraph in Dr. Higgins' fifth report, 1856, reading: "In no State has there been an office similar to this one for the benefit of agriculture in Maryland. The mere fact of an officer going through this State and discussing agricultural matters and directing public attention to them is productive of great good." Incidentally, is this the beginning of the experiment station and extension work in the country?

The Governor in April, 1848, appointed Dr. James Higgins, of Anne Arundel County, a graduate in medicine, 1839, of the University of Maryland, and a practicing physician, the first State agricultural chemist. Dr. Higgins held the position until May, 1858, when he was succeeded by Phillip T. Tyson of Baltimore. Dr. John Bickell was the first assistant State agricultural chemist.

During the ten years he held the position, Dr. Higgins published six reports, dealing with agricultural chemistry, analysis of soils, minerals and manures. As stated before, his analyses and discussions based thereon of plaster Paris, guano, dissolved bone, and manipulated fertilizers were the most potent factors in the revision of Maryland fertilizer laws, making them of real service to the people. I shall not take your time to discuss these various reports. They are interesting from many points of view to the soil and to the fertilizer chemist.

Reference may be made, perhaps, to one other point of historical interest. I have seen the statement in several places that Professor Samuel Johnson, of Connecticut, whose textbooks we older members of this Association used in college, introduced the valuation of fertilizers into this country. Indeed, Professor Johnson states in a report to the Connecticut State Board of Agriculture, in 1870: "When I first introduced the valuation of manures into this country in 1856 (apparently he had the thought in mind as early as 1853), following the example set by Stockhardt in Germany. . . ." As a matter of fact, Dr. Higgins introduced valuation of fertilizers as early as 1851. Under date of October 7, 1851, in a letter to Mr. J. Horner, of Baltimore, he says, in part: "Estimating Patagonian guano and your manure by the same rule as to the value of the several constituents, the Patagonian guano would be worth \$19.20 per ton, and your manure \$14.44. . . . The value of Patagonian guano and your manure I

determine by the aggregate value of their several valuable constituents, and by the same rule which would make Peruvian guano worth \$46.00 per ton."

In his second report, published January, 1852, about 20 pages are devoted to a discussion of guano, its fraudulent character, analysis, and valuation, and in this report Dr. Higgins acknowledges his indebtedness to Professor Way, of England, Chemist of the Royal Agricultural Society, who, he states, published a very able and elaborate paper on the composition and money value of different specimens of guano, in the Tenth Volume of the Journal of the Royal Agricultural Society. He states: "I refer to this paper with more pleasure as it confirms all the points urged by me in my last report (dated January 22, 1850). It confirms also the necessity for the action which I then urged on your honorable body."

David Stewart, Professor of Chemistry at St. John's College, Annapolis, and chemist for the Maryland State Agricultural Society, was also assigning monetary values to guanos and fertilizers as early as 1852.

An interesting thing, it seems to me, about the early agricultural chemists of this country is that while they seemed to know what was going on in Europe, they knew little about what was being done by other chemists in America, or chose to ignore it, I am uncertain which. So far I have found no reference to Dr. Johnson's work in Dr. Higgins' reports, nor do I find any reference to Dr. Higgins' work in Dr. Johnson's reports. It would seem that they should have known something about what each was doing since both of them were very active in agricultural chemical affairs in the early 1850's.

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## SEMIMICRO DETERMINATION OF HALOGENS IN ORGANIC COMPOUNDS

By E. P. CLARK (Insecticide Division, Bureau of Chemistry and Soils,  
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The following semimicro methods for the determination of halogens in organic compounds are the results of numerous experiments in which semimicro technic was applied to various standard macro methods. From the standpoint of general applicability, rapidity, accuracy, and simplicity, they are considered satisfactory and are presented here for consideration as possible material for inclusion in the official methods of the A.O.A.C.

Chlorine and bromine are determined by the Carius method. The procedure is essentially the same as that used in the macro system except that approximately 25 mg. samples are employed, which entails a corresponding refinement in weighing the sample and the resulting silver halide and the use of apparatus of appropriate size.

Specifications for such equipment are presented in Figs. 1, 2, and 3. The bomb furnace, Fig. 1, consists essentially of a cylindrical section of alumin-

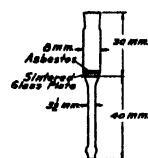
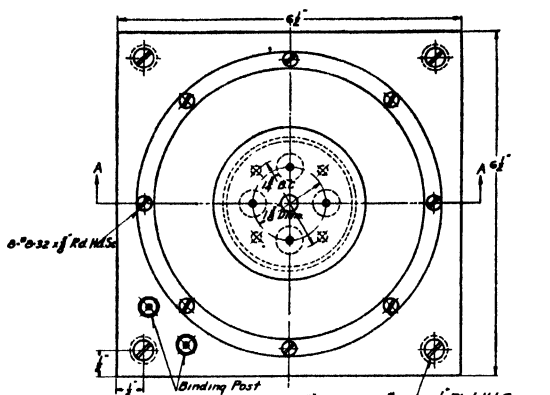


FIG. 3

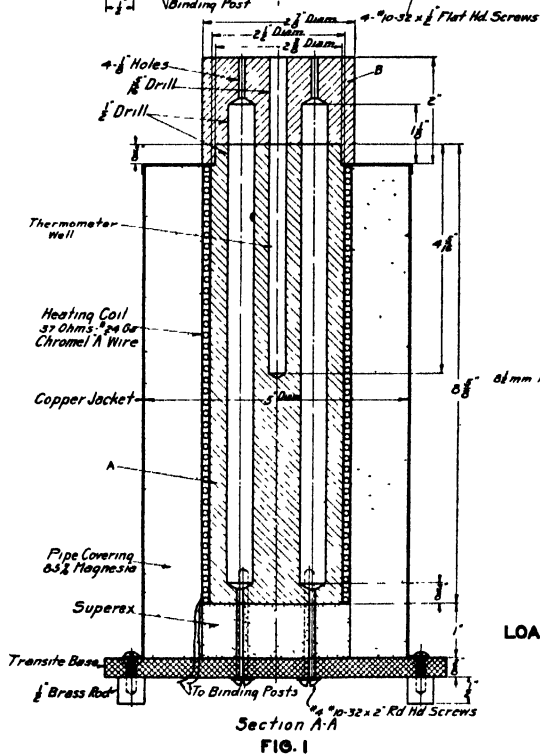


FIG. 1

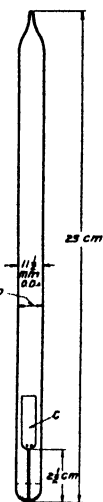
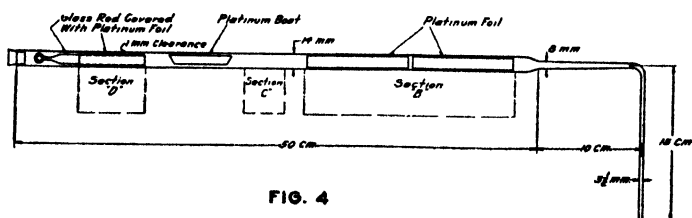

FIG. 2  
LOADED BOMB TUBE


FIG. 4

ium (A) provided with holes to contain the bomb tubes and thermometer. It is surrounded with a heating coil and insulator and is provided with a heavy, loose-fitting protective cap (B). Heat is supplied from a 110-volt power line and is regulated by a 45-ohm sliding resistance. Bomb tubes of either pyrex or soft glass constructed as indicated have never failed at 300°C. The design of the sample tube (C) with the small rod attached is chosen to prevent silver halides adhering to the bomb tube. This difficulty frequently occurs when an ordinary sample tube rests on the bottom of small-bore Carius tubes.

*Procedure.*—The bomb tube is charged with approximately 60 mg. of silver nitrate crystals and 0.3 cc. of fuming nitric acid. The sample tube, containing approximately 25 mg. of substance weighed to 0.02 mg.,<sup>1</sup> is inserted in the tube, which is then sealed and placed in the furnace. The length of the tube should be such that about 1 cm. of the sealed capillary end extends into the recess of the loose cap (B). The temperature of the furnace is gradually raised to 300° at which point it is kept for several hours. The usual procedure is to charge the furnace in the morning; bring it to the required temperature, which is maintained during the remainder of the working day; then allow it to cool during the night. The next morning the tube is opened,<sup>2</sup> and the silver halide is washed into a small beaker and transferred by the Pregl method<sup>3</sup> to a mat of asbestos in a small, sintered-glass Pregl tube (Fig. 3). The silver halide is well washed, first with water then with alcohol, and dried at 125°. The tube is removed from the oven, cooled to room temperature in the open, and weighed with the same precision that was used in weighing the sample. In this process another tube, prepared and treated exactly the same as the one containing the silver halide, is used as a tare. This operation compensates for moisture adsorbed by the asbestos pad and frequently eliminates an otherwise appreciable error.

The following results were obtained with this procedure.

SUBSTANCE	SAMPLE	Ag HALIDE	HALOGEN FOUND	HALOGEN CALCULATED
	mg.	mg.	per cent	per cent
p-Bromobenzoic acid	26.26	24.60	39.87	39.76
	28.87	27.00	39.89	
m-Bromonitrobenzene	28.22	26.26	39.60	39.57
	25.99	24.27	39.74	
m-Chlorbenzoylbenzoic acid	25.32	14.06	13.74	13.61
	22.86	12.66	13.70	
	25.92	14.33	13.68	

<sup>1</sup> The sample is most conveniently handled by weighing it as a pellet upon a small piece of cigarette paper from which it is transferred to the sample tube. The pellet may be made in any of the usual sample pill machines. See Pregl, *Quantitative Organic Microanalysis*, 2nd ed., p. 211. Translated by Fyfe (1930).

<sup>2</sup> The same precautions should be observed in opening the tubes as are used in the macro method. The cap B is carefully removed, and, with a hand torch, a small hot flame is applied to the sealed tip of the capillary. When the glass softens it is blown out as the internal pressure is released. The tube is then removed, scratched with a glass knife about two inches from the bottom and broken in the usual way with a hot tip of a glass rod.

<sup>3</sup> Ref. 1, page 133

*Iodine.*—Because it is considered that iodine in organic compounds is more conveniently and accurately determined by the Leipert volumetric method as given by Friedrich<sup>1</sup> than by other methods, this procedure is recommended. The method consists in burning the sample with oxygen in a platinum-filled combustion tube and collecting the liberated iodine in 5 per cent sodium hydroxide solution. The iodine is oxidized to iodate, which is reacted with an excess of potassium iodide, and the liberated iodine is determined with thiosulfate.

Specifications for the apparatus adapted to semimicro conditions are presented in Fig. 4. The combustion tubing is the same as that recommended for the determination of carbon and hydrogen and the fillings conform to the dimensions of the combustion furnace previously described by the writer.<sup>2</sup>

*Procedure.*—Approximately 25 mg. of material in a platinum boat is placed in the combustion tube and burned as described in the carbon and hydrogen determination. At frequent intervals a small flame is applied to the iodine, which collects in the cool portion of the constricted end of the combustion tube and is driven past the right-angled bend. When the combustion is completed and the tube (except the portion which dips into the alkali) is swept free of iodine, the connection to the oxygen supply is replaced by a small rubber tube; with slight suction from the mouth applied to the tube the alkali is drawn repeatedly over the iodine until it is dissolved. By the same procedure the tube is then washed several times with a few cc. of water. To the combined alkaline liquid and washings is added 10 cc. of a 10% solution of potassium acetate in glacial acetic acid containing 0.1 cc. of bromine (10 drops of bromine from a medicine dropper with a tip 2 mm. outside diameter and a 1 mm. bore). The liquids are thoroughly mixed and diluted to approximately 150 cc., after which the excess bromine is reduced with 15 to 20 drops of 90% formic acid. One gram of potassium iodide is then dissolved in the liquid, about 5 cc. of 10% sulfuric acid is added, and the liberated iodine is titrated with 0.05 *N* thiosulfate. One-sixth of the iodine liberated represents the iodine in the original sample.

The following example is presented.

5-Iodosalicylic acid	SAMPLE TAKEN	I	I
		FOUND	CALCULATED
	<i>mg.</i>	<i>per cent</i>	<i>per cent</i>
	21.42	48.23	48.07
	22.39	48.03	
	20.61	48.02	

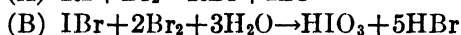
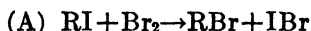
This method gave good results with all iodo compounds upon which it was tried. However, if the iodine is in aliphatic combination it is more convenient and rapid to use the principle outlined by Vieböck and Breckner,<sup>3</sup> which Vieböck and Schwappach<sup>4</sup> employed so effectively in their volumetric alkoxy determination. This method is based upon the following reactions:

<sup>1</sup> Die Praxis der Quantitativen Organischen Mikroanalyse, p. 102. (1933)

<sup>2</sup> This Journal, 16, 413 (1933).

<sup>3</sup> Pharm. Monats., 10, 191 (1929).

<sup>4</sup> Ber., 63, 2818 (1930).



After the reaction is completed the iodine is determined in the same manner as outlined in the combustion method. The procedure follows:

Approximately 20 mg. of substance is weighed upon a tared piece of cigarette paper  $12 \times 25$  mm. The paper and its contents are placed in a  $25 \times 140$  mm. test tube, and 10 cc. of a 10% solution of potassium acetate in glacial acetic acid containing 0.1 cc. of bromine is added. If the sample dissolves immediately it is allowed to stand for 5 min. after which the liquid is heated to boiling and allowed to stand for 15 min. longer. If the sample does not dissolve readily, it is heated at once and allowed to stand for 15 min. Liquids are conveniently weighed in sealed, small bore, melting-point tubes, which are then crushed in the bromine reagent. From this point the procedure is the same as that for solids. After the indicated time, 125 cc. of water is used to wash the reaction mixture into a flask containing 5 cc. of a 25% aqueous sodium acetate solution. Eighteen drops of 90% formic acid are then added to reduce the excess bromine, after which 1 gram of potassium iodide and a few cc. of 10% sulfuric acid are added. The liberated iodine is titrated with 0.05 *N* thio-sulfate, one-sixth of which represents the quantity of iodine in the sample.

A few analyses made on approximately 20 mg. samples are presented in the following table.

SUBSTANCE	IODINE CALCULATED	IODINE FOUND
	per cent	per cent
Iodoacetic acid	68.24	68.32
B-Iodopropionic acid	63.46	63.54
		63.58
Methylene iodide	94.75	94.73
Iodoform	96.69	96.73
		96.72
Stearyl iodide	33.37	33.40

## COMPOSITION AND PROPERTIES OF SUPERPHOSPHATE

### I. DETERMINATION OF WATER IN SUPERPHOSPHATE AND THE RELATION BETWEEN FREE WATER AND FREE ACID\*

By W. L. HILL and K. D. JACOB (Fertilizer Investigations, Bureau of Chemistry and Soils, Washington, D. C.)

Since the beginning of the chemical fertilizer industry it has been customary to consider the calcium sulfate constituent of superphosphate as being completely hydrated to the dihydrate (gypsum).<sup>1</sup> However, the presence of gypsum in superphosphate has never been shown by experiment, and recently Krügel and Retter,<sup>2</sup> in an effort to account for all the

\* Presented at the Annual Meeting of the Association of Official Agricultural Chemists, held at Washington, D.C., November, 1933.

<sup>1</sup> Waggaman and Easterwood, *Phosphoric Acid, Phosphates and Phosphatic Fertilizers*, p. 164, Chemical Catalog Co. (1927); Schucht, *Die Fabrikation des Superphosphates*, p. 69. Vieweg und Sohn (1928).

<sup>2</sup> *Superphosphate*, 3, 57 (1930).

water known to be present in a sample of superphosphate, concluded that only about one-seventh of the calcium sulfate could be present as the dihydrate. Considerations such as these prompted the initiation in this Bureau of a study of the state of hydration of the calcium sulfate in superphosphate, or more generally, the distribution of the water among the more important constituents of superphosphate. A method to determine the hygroscopic or free water in the material fairly accurately was considered indispensable, as was also some way of determining the total water of crystallization. Therefore, it was necessary to study with some care several methods that have been used for the determination of water in superphosphate. The results are reported in this paper.

### GENERAL CONSIDERATIONS

The term *superphosphate*, as used in this paper, includes (1) *ordinary superphosphate*, containing approximately 18 to 20 per cent of phosphoric oxide ( $P_2O_5$ ) and made by treating phosphate rock, or bone, with sulfuric acid; and (2) *double superphosphate* (also called triple or treble superphosphate), containing about 45 to 50 per cent of phosphoric oxide and made by treating phosphate rock, or bone, with phosphoric acid. These terms also refer only to materials that have not been mixed with ground limestone, sand, or other "conditioners" and "fillers."

The predominant constituent of double superphosphate is monocalcium phosphate monohydrate, whereas ordinary superphosphate contains both monocalcium phosphate monohydrate and calcium sulfate as major constituents.<sup>1</sup> As already indicated, there is some uncertainty concerning the condition of the calcium sulfate in superphosphate; however, x-ray diffraction studies<sup>1</sup> made in this Bureau indicate that anhydrous calcium sulfate is the predominant form, and that if the dihydrate is present in commercial superphosphate at all, the amounts must be less than 2 to 3 per cent of the sample. A small quantity of dicalcium phosphate dihydrate is indicated in only one of the superphosphates examined by Hendricks thus far. Superphosphate also contains fluorine compounds, concerning which little is known at present, in amounts equivalent to 1 to 3 per cent of fluorine. Although the fluorine-bearing constituents may or may not contain water, there is the possibility that in contact with free phosphoric acid they will decompose, at least in part, and through the liberation of volatile fluorine acids cause erroneous results in the water determination. Other constituents that may have some slight bearing on the water determination, such as small quantities of unattacked phosphate rock, silicates, and iron and aluminum compounds, will not be considered at this time.

The water in superphosphate evidently exists in three different states: (1) water of constitution, as in  $H_3PO_4$  and  $Ca(H_2PO_4)_2 \cdot H_2O$ , (2) water of

<sup>1</sup> S. B. Hendricks, unpublished data.

crystallization, as in  $\text{Ca}(\text{H}_2\text{PO}_4)_2 \cdot \text{H}_2\text{O}$ , and (3) hygroscopic or free water, the larger part of which exists on the surface of the solid particles in the form of a solution of the superphosphate constituents. For convenience this solution of the superphosphate constituents in the hygroscopic water is called the *superphosphate solution*, and as used in this paper the terms *hygroscopic water* and *free water* are interchangeable.

The superphosphate solution always contains more or less so-called free acid, principally phosphoric acid. Fluorine acids, and in ordinary superphosphate also sulfuric acid, are doubtless present, though in relatively small quantities. The negative radicals present in the superphosphate solution, for the purpose of this paper, are designated as the corresponding acids. The quantities of sulfuric acid falling in this classification can be roughly estimated from existing data<sup>1</sup> on the composition of solutions in equilibrium with calcium sulfate dihydrate and hydrated monocalcium phosphate. Thus, the sulfate content of the superphosphate solution of a material containing 5 per cent each of free water and free acid should be equivalent to about 0.002 per cent of  $\text{H}_2\text{SO}_4$ ; if the free water and acid were 8.2 and 1.8 per cent, respectively, a total of 10 per cent as before, the  $\text{H}_2\text{SO}_4$  should amount to about 0.007 per cent. Fluorine acids equivalent to at least 0.02 to 0.07 per cent of fluorine are indicated by analysis of ether extracts of superphosphate (Tables 9 and 10).

As phosphoric acid is the predominant acid in the superphosphate solution, this solution may be regarded as a phosphoric acid solution of the several solid constituents of the superphosphate; its composition probably varies from point to point in the sample, and also from layer to layer on a given solution-coated particle. Nevertheless, it is possible to estimate on a statistical basis the relative quantities of calcium, for example, that may be dissolved in the superphosphate solution. Cameron and Bell<sup>2</sup> found that the calcium and phosphoric oxide concentrations of solutions in contact with solid calcium phosphate are practically the same whether solid calcium sulfate dihydrate is present or not. Thus, sulfates may be neglected as a factor determining the calcium content of the superphosphate solution. Then, if the effects (probably small) of the minor constituents, such as fluorine, iron and aluminum, are disregarded, the quantity of calcium in solution may, as a first approximation, be considered as dependent upon the solubility of monocalcium phosphate (always present in superphosphate in large excess) in aqueous phosphoric acid. With this thought in mind the writers calculated the solubility of hydrated monocalcium phosphate in aqueous phosphoric acid from Bassett's data.<sup>3</sup> The results are shown in Fig. 1.

Accordingly, 1 gram of 60 per cent phosphoric acid, when saturated at 25°C. with respect to monocalcium phosphate, contains about 12 mg. of

<sup>1</sup> Cameron and Bell, *J. Am. Chem. Soc.*, 28, 1222 (1906).

<sup>2</sup> *Loc. cit.*

<sup>3</sup> *Z. anorg. Chem.*, 59, 1-55 (1908).



calcium, whereas a like quantity of a 20 per cent acid under the same conditions contains almost five times more calcium. Similar variations in the calcium content of the superphosphate solution are to be inferred, and the actual quantity of calcium in solution will depend not only upon the total quantities of free water and free phosphoric acid, but also upon their relative amounts. In a superphosphate that contains 4 per cent free phosphoric acid and 6 per cent free water (which corresponds to 0.1 gram of 40 per cent aqueous  $\text{H}_3\text{PO}_4$  per gram of superphosphate), as much as 3.3 mg. of Ca per gram of superphosphate may be dissolved in the superphosphate solution.

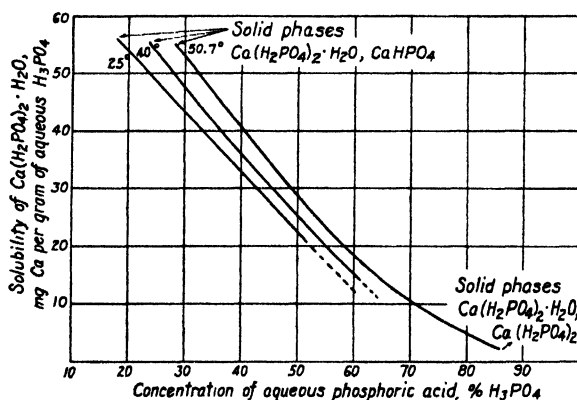


Fig. 1. — Solubility of hydrated monocalcium phosphate in aqueous phosphoric acid.

The significance of this relatively small quantity of calcium can be better appreciated when it is considered in the light of the alterations in the relative quantities of acid and water in the superphosphate solution that may occur during the deposition of the dissolved calcium—a process that always takes place to a greater or less extent during the determination of water or free acid. In this connection it will be convenient to discuss equilibrium mixtures of hydrated monocalcium phosphate and phosphoric acid obtained by adding known quantities of water and acid to monocalcium phosphate at 25°C. If in the analytical determination of the added water and acid the dissolved calcium precipitates as  $\text{Ca}(\text{H}_2\text{PO}_4)_2 \cdot \text{H}_2\text{O}$ , complete recovery can be accomplished. On the other hand, if the calcium separates as dicalcium phosphate, the recovered acid will be greater, and depending upon whether the anhydrous or hydrated salt separates the water will be greater or less than the amount added. The relationship between the observed values for free water and free acid in such mixtures, as it may be effected by the behavior of the dissolved calcium at three points on the solubility curve at 25°C. (Fig. 1), is shown in Fig. 2. If some of all three salts were deposited, the observed value would corre-

spond to a point within a triangle whose vertices lie on the three curves, respectively. Owing to the greater solubility of monocalcium phosphate in the more dilute phosphoric acid, the differences become more and more pronounced as the relative amount of water is increased. On the other hand, when the quantity of free water is very small in relation to the free acid, the observed values should, on account of the reduced solubility of the calcium, be practically independent of the form in which the dissolved calcium separates. Furthermore, if small quantities of fluorine

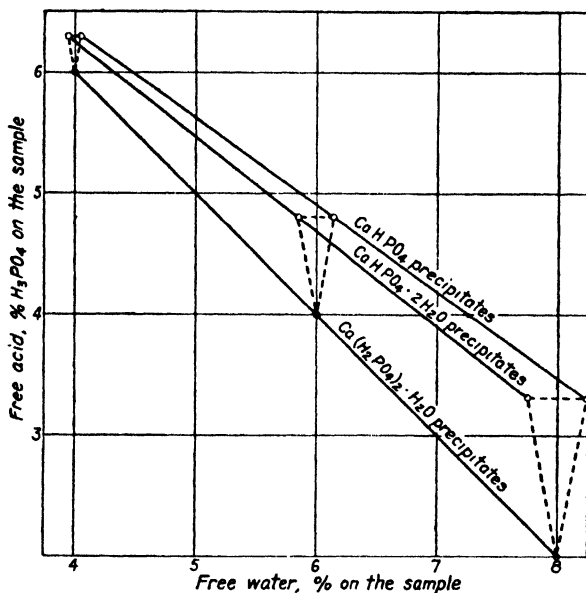


Fig. 2. - Effect of the form in which the dissolved calcium precipitates on the observed values for free water and free acid in monocalcium phosphate.

acids, for example, hydrofluoric acid, were present, these differences (Fig. 2) would in all probability be minimized, and with sufficient fluorine completely eliminated, as a result of the separation of calcium fluoride.

It is obvious that at best the analytical results for free water, or free acid, do not represent the actual quantity that may be present in the superphosphate solution, but rather the amount of water, or acid, in excess of that carried down in the deposited salts. Furthermore, this excess cannot be regarded as a definite quantity until the composition of the deposited salts is fixed. For this reason it will be convenient to define the *free water* in superphosphate as the water (exclusive of water of constitution, as in  $\text{H}_3\text{PO}_4$ ) in the superphosphate solution in excess of that required as crystal water by the salt, or salts, precipitated during the analytical operation, when, and only when, the precipitated salts are those that

are stable in contact with the superphosphate solution at the beginning of the determination. A similar situation holds for the free acid, but owing to the presence of small quantities of acids other than phosphoric, which form slightly soluble calcium salts, the free acid must be regarded as the phosphoric acid equivalent of the total free acid. Then, if aqueous phosphoric acid having the same  $\text{H}_3\text{PO}_4\text{-H}_2\text{O}$  ratio was actually restored to the material from which the free water and acid had been removed by a suitable method the relationships of the resulting mixture, as regards the composition of the solution phase in particular, presumably would sooner or later approach closely those prevailing in the original superphosphate. Moreover, by conversion of the properly determined values for free water and free acid into terms of aqueous phosphoric acid, it is possible with the aid of the solubility curves (Fig. 1) to determine the calcium phosphate that is most probably stable in contact with the superphosphate solution. Accordingly, at  $25^\circ\text{C}$ . hydrated monocalcium phosphate is to be regarded as the stable calcium phosphate in contact with superphosphate solutions whose free water and free acid contents correspond to aqueous phosphoric acid ranging from about 17 to above 60 per cent  $\text{H}_3\text{PO}_4$ . The concentrations of free acid in all superphosphates for which data are available fall well within this range.

#### MATERIALS

Unless it is otherwise indicated, the pure compounds used in this study were prepared by the writers; they were also checked by chemical analysis, as well as by x-ray and microscopic examinations.

Samples 1315 and 1316 are ordinary superphosphates prepared commercially during 1933 from Florida land-pebble and Tennessee brown-rock phosphates, respectively. Samples 1320 and 1066 are ordinary superphosphates prepared commercially about 1930 from Florida land-pebble and Tennessee brown-rock phosphates, respectively. Samples ES-IA and ES-IB are ordinary superphosphates prepared in the laboratory from C.P. tricalcium phosphate and sulfuric acid by a method<sup>1</sup> that with phosphate rock yields a product that is very similar to commercial superphosphate. Samples 1337 and 1338 are double superphosphates prepared commercially during 1933 from Florida land-pebble phosphate and phosphoric acid produced by the sulfuric acid process. A small quantity of crude mineral oil was added to eliminate excessive foaming during the manufacture of the phosphoric acid used in the preparation of No. 1338. Mineral oil was not added in any stage of the manufacture of No. 1337. All the superphosphate samples were ground to pass a 20-mesh sieve.

#### METHODS FOR DETERMINING WATER

The methods that have been used for the determination of water, com-

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<sup>1</sup> Private communication from H. C. Moore, Armour Fertiliser Works, Atlanta, Ga.

monly termed "moisture," in superphosphate may be classified as (1) drying methods, (2) distillation methods, and (3) extraction methods.

Oven drying as used in the official methods<sup>1</sup> of this and many foreign countries is by far the most common procedure. Other procedures in which simple drying is used include exposure to a stream of dry air<sup>2</sup> at 0°C. and desiccator methods, for example, desiccation at room temperature over phosphoric oxide at atmospheric pressure,<sup>3</sup> over concentrated sulfuric acid under reduced pressure,<sup>4</sup> and the novel method of Wickern.<sup>5</sup>

In the distillation methods the sample is boiled with an organic liquid in a special apparatus, for example, that of Bidwell and Sterling,<sup>6</sup> and the volume of the water distilled over is measured in a graduated receptacle. For this purpose benzene<sup>7</sup> and toluene<sup>8</sup> have been used at various times.

Extraction methods involve an extraction of the sample with a suitable non-aqueous solvent capable of removing the free water and the determination of both the total weight extracted and the amount of material other than water that is removed from the sample. Methods based on this principle are closely related to, and in fact inseparable from, methods for determining free acid. The liquids used in the water determination include absolute alcohol, as in Schucht's method,<sup>9</sup> and ether which, so far as the writers are aware, is for the first time proposed in this paper.

It will be convenient to discuss various features of the several methods studied as the data showing their performance both on pure materials and superphosphates are presented. Unless it is otherwise stated, the size of the sample was 2 grams, platinum ware was the rule, and desiccators containing sulfuric acid (sp. gr. 1.84) were used.

#### DRYING METHODS

In the determination of any form of water in superphosphate by any method, due regard must be given to the behavior of the free phosphoric acid and its effect on the nature of the various changes which may be operative in the superphosphate. When it is concentrated by the removal of water in the drying process, for example, the phosphoric acid will react in part with certain other constituents, such as small amounts of unattacked rock, any dicalcium phosphate that may be present, fluorine compounds, hydrated salts, etc., with the consequence that the loss in weight of the sample represents a net result of various ill-defined changes and in addition to so-called moisture may also include crystal water and volatilized fluorine compounds. Moreover, that portion of the free phosphoric

<sup>1</sup> *Methods of Analysis, A.O.A.C.*, 1930, 14; Wiley's Principles and Practice of Agricultural Analysis, Vol. II, pp. 33-40, Chemical Publishing Co. (1931).

<sup>2</sup> Private communication from C. C. Howes, Davison Chemical Co., Baltimore, Md.

<sup>3</sup> Caldwell, *Cotton Oil Press*, 7, No. 11, 35 (1924).

<sup>4</sup> Private communication from W. H. MacIntire, Agr. Expt. Sta., Knoxville, Tenn.

<sup>5</sup> *Chem.-Ztg.*, 57, 221 (1933).

<sup>6</sup> *Ind. Eng. Chem.*, 17, 147 (1925).

<sup>7</sup> Krügel and Retter, *Superphosphate*, 3, 57 (1930).

<sup>8</sup> Smith, *This Journal*, 16, 220 (1933).

<sup>9</sup> *Die Fabrikation des Superphosphates*, p. 293, Vieweg und Sohn (1926).

acid escaping the reactions just mentioned may itself lose water of constitution above 100°C. to form pyrophosphoric acid.<sup>1</sup>

If the complications occasioned by the free acid are disregarded, the fact that monocalcium phosphate loses its water of crystallization<sup>2</sup> at 100°C., as does also calcium sulfate dihydrate (Table 2), would indicate that oven drying at about this temperature might, if the loss of fluorine is not too great, give an approximate value for the sum of the free water and water of crystallization. With this in mind the writers determined the loss in weight of samples dried at 120°, 105° and 80°C., respectively, in a well-ventilated electric oven on the superphosphates (Tables 1 and 11), and also on pure compounds (Table 2) that are possible constituents of superphosphate. These determinations were made one at a time, the sample being placed immediately below and almost touching the thermometer bulb, and the drying was continued until constant weight was attained, or until the loss on drying an additional 3 hours was less than 1 mg. In the case of ordinary superphosphate 18 to 20 hours, or even less, is usually sufficient (Table 1).

TABLE 1.—*Effect of temperature and period of drying on the weight lost by ordinary superphosphates*

TIME	LOSS IN WEIGHT OF—					
	FLORIDA LAND-PEBBLE SUPERPHOSPHATE NO. 1315 AT—			TENNESSEE BROWN-ROCK SUPERPHOSPHATE NO. 1066 AT—		
	120°C.	105°C.	80°C.	120°C.	105°C.	80°C.
hours	per cent	per cent	per cent	per cent	per cent	per cent
3	8.43	8.18	7.00	7.82	6.15	4.57
5	8.85	8.26	7.10	8.50	6.40	4.67
23	9.43	8.46	7.30	9.18	6.80	4.92
27	9.45	8.46	7.33	9.18	6.85	4.92

TABLE 2.—*Loss in weight of pure materials dried in oven at different temperatures*

MATERIAL	FREE ACID AS H <sub>3</sub> PO <sub>4</sub>	THEORETICAL WATER OF CRYSTALLIZA- TION	LOSS IN WEIGHT WHEN DRIED IN OVEN AT—		
			120°C.	105°C.	80°C.
	per cent	per cent	per cent	per cent	per cent
Ca(H <sub>2</sub> PO <sub>4</sub> ) <sub>2</sub> · H <sub>2</sub> O	0.00	7.14	7.41 <sup>a,e</sup>	7.23 <sup>b,e</sup>	0.20 <sup>b,f</sup>
CaHPO <sub>4</sub> · 2H <sub>2</sub> O, Kahlbaum	0.00	20.93	10.84 <sup>a,e</sup>	10.45 <sup>d,e</sup>	4.19 <sup>b</sup>
CaSO <sub>4</sub> · 2H <sub>2</sub> O	0.00	20.92	20.42 <sup>a,e</sup>	20.03 <sup>b,e</sup>	6.25 <sup>b,f</sup>
H <sub>3</sub> PO <sub>4</sub> , C.P.	86.6	13.40	14.19 <sup>b,e</sup>	12.92 <sup>b,e</sup>	10.89 <sup>b,e</sup>
Ca(H <sub>2</sub> PO <sub>4</sub> ) <sub>2</sub> · H <sub>2</sub> O + CaSO <sub>4</sub> · 2H <sub>2</sub> O <sup>h</sup>	0.00	14.14	14.13 <sup>a</sup>	14.16 <sup>b,f</sup>	—
Ca(H <sub>2</sub> PO <sub>4</sub> ) <sub>2</sub> · H <sub>2</sub> O + CaSO <sub>4</sub> · 2H <sub>2</sub> O + H <sub>3</sub> PO <sub>4</sub> <sup>h</sup>	5.00	14.14	15.32 <sup>b,f,g</sup>	13.94 <sup>b,e,g</sup>	—

<sup>a</sup> Dried 3 hours.

<sup>b</sup> Dried 24 hours.

<sup>c</sup> Dried 65 hours.

<sup>d</sup> Dried 120 hours.

<sup>e</sup> Apparent constant weight.

<sup>f</sup> Still losing weight.

<sup>g</sup> Excluding the water added with the acid.

<sup>h</sup> Equal weights of Ca(H<sub>2</sub>PO<sub>4</sub>)<sub>2</sub> · H<sub>2</sub>O and CaSO<sub>4</sub> · 2H<sub>2</sub>O.

<sup>1</sup> Balareff, *Z. anorg. Chem.*, **67**, 234 (1910).

<sup>2</sup> Stoklass, *Z. anal. Chem.*, **29**, 390 (1890).

Although it might be suspected that the water removed from superphosphate by drying at room temperature, or below, is largely free water this is not necessarily the case (Table 3). The results obtained by drying

TABLE 3.—*Effect of drying certain hydrates at 25° C.*

COMPOUND	BEHAVIOR OF WATER OF CRYSTALLIZATION WHEN SALT IS STORED OVER CONCENTRATED SULFURIC ACID AT—	
	ATMOSPHERIC PRESSURE	100 MM.
Ca(H <sub>2</sub> PO <sub>4</sub> ) <sub>2</sub> · H <sub>2</sub> O, acid-free	Keeps indefinitely <sup>a</sup>	No loss in 10 days
with H <sub>3</sub> PO <sub>4</sub> <sup>b</sup>	No loss in several weeks	Lost 0.06% in 3 hours, 1.06% in 20 hours
CaHPO <sub>4</sub> · 2H <sub>2</sub> O, Kahlbaum, acid-free	No loss in 4 days	—
with H <sub>3</sub> PO <sub>4</sub> <sup>b</sup>	Reacts to form Ca(H <sub>2</sub> PO <sub>4</sub> ) <sub>2</sub> · H <sub>2</sub> O with liberation of 1 mole of crystal water	
CaSO <sub>4</sub> · 2H <sub>2</sub> O, acid-free	No loss in 7 days <sup>c</sup>	No loss in 9 days
with H <sub>3</sub> PO <sub>4</sub> <sup>b,d</sup>	Lost water rapidly at first and appeared to pass to the hemi-hydrate	

<sup>a</sup> Birnbaum, *Z. Chem.*, [2] 7, 137 (1871).

<sup>b</sup> Sufficient 40% phosphoric acid was added to yield a mixture containing 5% of free H<sub>3</sub>PO<sub>4</sub>. The mixture was flooded with ether, stirred well, and when the odor of ether had disappeared, it was placed in the desiccator.

<sup>c</sup> According to Whittaker, et al (*Ind. Eng. Chem.*, 25, 1280 (1933)) a sample of CaSO<sub>4</sub> · 2H<sub>2</sub>O lost 1.1% of its weight "on being brought to apparent constant weight over P<sub>2</sub>O<sub>5</sub>" (about 7 weeks).

<sup>d</sup> Also lost water of crystallization, though much less rapidly, when exposed to a current of dry (Dehydrite) air at 0°C.

ordinary superphosphate 18 to 24 hours in a stream of dry (Dehydrite) air agreed closely (Table 2) with those obtained when the sample was desiccated for 48 hours at atmospheric pressure over concentrated sulfuric acid. The rate at which ordinary superphosphates lose weight when dried singly at 25°C. over concentrated sulfuric acid at atmospheric pressure

TABLE 4.—*Rate of loss in weight of ordinary superphosphates over concentrated sulfuric acid at 25°C.*

TIME	LOSS IN WEIGHT OF—					
	FLORIDA LAND-PEBBLE SUPERPHOSPHATE NO. 1315 AT—		FLORIDA LAND-PEBBLE SUPERPHOSPHATE NO. 1320 AT—		TENNESSEE BROWN-ROCK SUPERPHOSPHATE NO. 1316 AT—	
	ATMOSPHERIC PRESSURE	100 MM.	ATMOSPHERIC PRESSURE	100 MM.	ATMOSPHERIC PRESSURE	100 MM.
hours	per cent	per cent	per cent	per cent	per cent	per cent
3	5.65	6.29	—	1.53	5.20	5.89
5	6.05	6.44	1.30	1.58	5.65	6.06
24	6.79	6.74	1.35	—	6.10	6.49
48	6.87	6.96	1.43	—	6.30	6.59
72	6.85	7.11	1.53	1.85	6.48	—

and also under reduced pressure is shown in Table 4. As monocalcium phosphate in contact with free phosphoric acid loses crystal water (Table 3) to concentrated sulfuric acid in an evacuated desiccator, a superphosphate should not be dried in this manner longer than about 3 hours. Results obtained by the desiccator methods on all the materials are collected in Table 11.

#### DISTILLATION METHODS

Five grams of the sample was boiled for 30 minutes with benzene in an apparatus similar to the one described by Bidwell and Sterling.<sup>1</sup> Most of the water was given off during the first 10 to 15 minutes of boiling, and results obtained on superphosphate by boiling 60 minutes were not appreciably higher than those obtained in 30 minutes. Considerable annoyance was experienced with drops of water clinging to the sides of the trap, particularly during the later stages of boiling, and this occurred regardless of the care taken in cleaning the apparatus. As this difficulty was not experienced in the treatment of fluorine-free materials, it was attributed to volatilized fluorine compounds, the presence of which was indicated by etching of the apparatus.

Although Krügel and Retter<sup>2</sup> claim that the hygroscopic water in superphosphate can be accurately determined by distillation with benzene, this method has not proved satisfactory in the writers' hands. Aside from the difficulty mentioned in the preceding paragraph, the results in Table 5 indicate that crystal water is expelled from pure monocalcium phosphate when it is treated in this manner. Furthermore, the collected data (Table 11) show that this method, when applied to superphosphate, gives practically the same results as does oven drying at 80°C., which is approximately the boiling point of benzene.

TABLE 5.—*Loss of water of crystallization from monocalcium phosphate monohydrate and calcium sulfate dihydrate by distillation methods*

TIME	WATER EVOLVED FROM—				
	Ca(H <sub>2</sub> PO <sub>4</sub> ) <sub>2</sub> · H <sub>2</sub> O <sup>a</sup> WHEN BOILED WITH—			CaSO <sub>4</sub> · 2H <sub>2</sub> O <sup>a</sup> WHEN BOILED WITH—	
	BENZENE	TOLUENE	XYLENE	BENZENE	TOLUENE
minutes	per cent	per cent	per cent	per cent	percent
15	3.0	1.5	7.0	—	15.0
30	3.5	2.2	7.8	0.0	18.5
45	3.7	3.0	7.9	4.0	19.0
60	—	3.6	7.9	4.7	19.9
75	4.0	4.0	—	—	20.0

<sup>a</sup> Theoretical water of crystallization: Ca(H<sub>2</sub>PO<sub>4</sub>)<sub>2</sub> · H<sub>2</sub>O 7.14 per cent, CaSO<sub>4</sub> · 2H<sub>2</sub>O 20.92 per cent.

It was thought that by using a liquid with a higher boiling point, for example, toluene or xylene, the water of crystallization and hygroscopic

<sup>1</sup> *Ind. Eng., Chem.*, 17, 147, (1925).

<sup>2</sup> *Superphosphate*, 3, 57 (1930).

water might be determined together, but the results (Table 5) obtained on pure compounds indicate that the behavior of monocalcium phosphate in boiling toluene (111°C.) is about the same as in benzene, whereas water of constitution is evidently lost when xylene (b. p. about 140°C.) is used.

#### EXTRACTION METHODS

In view of the intimate relation between free water and free acid in the superphosphate solution, it would appear that an accurate determination of free water would involve the simultaneous removal of both constituents from contact with the superphosphate. In general, the success of extraction methods for the determination of hygroscopic water in superphosphate depends, therefore, upon the fact that the extracted sample, being devoid of free acid and water, can be brought to a definite condition for weighing. However, the principal difficulty in such methods lies in the determination of the quantity of material other than water that is removed by the extractant. In the alcohol method<sup>1</sup> this material is determined gravimetrically by drying to constant weight at 120°C. the residue obtained from the evaporation of the filtered extract. Owing to the fact already mentioned that phosphoric acid loses water of constitution above 100°C., this operation may be subject to appreciable error. In the ether method, which allows the determination of both water and free acid in one operation, the ether-soluble material other than water and phosphoric acid is neglected. A decision upon the accuracy of these methods cannot be made without access to rather detailed experimental data.

*Extraction with alcohol.*—When monocalcium phosphate, to which known quantities of free water and acid had been added as aqueous phosphoric acid, was treated with absolute alcohol according to Schucht's method, the amounts of water and acid removed by the alcohol were appreciably greater than were actually present in the untreated material (Table 6). The positive errors in the figures for free phosphoric acid and free water indicate the formation of anhydrous dicalcium phosphate (Fig. 2). In order to test this possibility, a portion of the acid used in the recovery experiment was saturated at 25°C. with monocalcium phosphate, and 1 ml. of this solution in contact with a very small excess of the solid salt was treated with sufficient absolute alcohol to make the ratio of alcohol to aqueous acid the same as that used in the recovery experiment. The precipitate was filtered, washed twice with alcohol, and exposed to the air 1 hour. Examination by the x-ray diffraction method<sup>2</sup> showed this material to be anhydrous dicalcium phosphate. As the concentration (about 39 per cent) of the aqueous acid was approximately in the middle of the range (Fig. 1) in which monocalcium phosphate is the stable salt, the deposition of the dissolved calcium as dicalcium phosphate is regarded

<sup>1</sup> Schucht, *Die Fabrikation des Superphosphates*, p. 293. Vieweg and Sohn (1926); Wiley's *Principles and Practice of Agricultural Analysis*, Vol. II, p. 35. Chemical Publishing Co. (1931).

<sup>2</sup> S. B. Hendricks kindly made the examination.





as an effect of the dilution of the aqueous solution phase with alcohol, whereby the concentration of phosphoric acid becomes less than is necessary to prevent the precipitation of the dicalcium salt. Absolute alcohol, being a dehydrating agent, would promote the formation of the anhydrous salt.

The fact that dicalcium phosphate is deposited under these conditions casts some doubt upon alcohol extraction as a satisfactory method for determining water in superphosphate. Nevertheless, the quantities of fluorine acids present in the superphosphate solution may be sufficient to precipitate the calcium and thus eliminate this difficulty. Although the alcohol extraction employed in the water determination is not identical with that used in determining free acid, the difference is only a matter of detail, and it is to be expected that the difficulty encountered here (Table 6) also exists in the determination of free acid by the alcohol method recently studied by Ross and Beeson.<sup>1</sup>

Fluorine was not found in the alcohol extracts of superphosphate (Table 10), but the filtered extracts carried elements of the  $R_2O_3$  group which probably passed the filter in colloidal condition. The extract of superphosphate No. 1338 contained 0.11 per cent (on the superphosphate) of  $R_2O_3$  as phosphates.

*Extraction with ether.*—The sample was extracted 3 to 18 hours (Table 8) with 100 ml. of dry alcohol-free ether<sup>2</sup> in a small Soxhlet apparatus, and the acid thus removed from the sample was determined<sup>3</sup> in the extract by distilling off the ether and titrating the filtered aqueous solution (volume 100 ml.) of the ether-soluble material with 0.1 N alkali, alizarin<sup>4</sup> being used as an indicator. The positive titration error, 0.01 to 0.05 ml. of alkali, was determined by titrating under the same conditions an equivalent amount of  $KH_2PO_4$ , and the result was corrected accordingly. A platinum, or porcelain, Gooch crucible was used as an extraction vessel, the sample being weighed directly into a crucible prepared as follows:

A circle of wet filter paper, having a diameter 1 to 2 mm. larger than the inside diameter of the bottom of the crucible, was carefully fitted in the crucible under suction, and a perforated plate was pressed into place to hold the edge of the paper firmly against the side of the vessel. The filter was washed with alcohol and then with ether, exposed to the air until free of ether, and allowed to stand in a desiccator over concentrated sulfuric acid 3 hours before weighing. (Experience has shown that the perforated plate can be omitted in most instances.) During extraction a shallow paper extraction thimble, which rested on top of the crucible, received the dripping ether and thus prevented spattering. When the extraction was finished, the crucible with its contents was kept in the open

<sup>1</sup> *This Journal*, 17, 238 (1934).

<sup>2</sup> The reagent grade of ether was washed 3 or 4 times with distilled water, stored over solid potassium hydroxide for several days, and filtered for use.

<sup>3</sup> Hersfelder, *Analyst*, 28, 372 (1903).

<sup>4</sup> Guthrie and Ramsay *J. Proc. Roy. Soc. N. S. Wales*, 43, 69 (1909).

at a temperature of about 35°C. until the odor of ether disappeared, and was then stored in a desiccator 3 hours before the final weight was taken. In routine determinations a shorter time in the desiccator would be sufficient in most cases, for the differences thus far observed between the weights after 30 minutes and 3 hours, respectively, amount to only 0.02 to 0.05 per cent, and additional losses on standing 48 hours were 0.00 to 0.07 per cent. The result for water was obtained by deducting the  $H_3PO_4$  equivalent of the titer from the total weight extracted from the sample.

Free water, as well as free phosphoric acid, can be satisfactorily determined by this procedure when monocalcium phosphate is the only solid compound present (Table 7). Under certain conditions this is also true when calcium sulfate is the solid phase. Furthermore, as shown by x-ray diffraction methods, when monocalcium phosphate containing free phosphoric acid is extracted with ether, the dissolved calcium separates as hydrated monocalcium phosphate (Fig. 2).

The data given in Table 8 are representative of the results obtained by extracting superphosphates with ether for different periods of time. Although prolonged extraction increases the amount of acid removed from the sample, particularly in the case of the old superphosphates, the results for water are little affected, and by speeding up the rate of flow of the ether the extraction, so far as it concerns water, can be completed in 3 hours.

TABLE 8.—*Effect of time of extraction on the results for water in ordinary superphosphates as determined by extraction with ether*

SAMPLE	SUPERPHOSPHATE MADE FROM—	TIME	LOSS IN WEIGHT OF SAMPLE	$H_3PO_4$ EQUIVALENT OF TITER	WATER
		hours	per cent	per cent	per cent
1316	Tennessee brown-rock phosphate	3 <sup>a</sup>	10.52	4.81	5.71
		5	10.53	4.88	5.65
		18	10.56	4.85	5.71
1320	Florida land-pebble phosphate	3 <sup>a</sup>	2.61	1.35	1.26
		5	2.69	1.37	1.32
		18	2.81	1.52	1.29
ES-IA	Tricalcium phosphate, C. P.	3 <sup>a</sup>	3.16	1.01	2.15
		5	3.19	0.98	2.21
		18	3.20	1.06	2.14

<sup>a</sup> Ether siphoned over 15 to 20 times per hour, whereas in the other determinations the rate was 10-12 times per hour.

Sulfuric acid was not detected in the ether extract of any air-dried superphosphate used in this study. These negative results were not unexpected, because, as already pointed out, previous data indicated that the quantity of sulfate in the superphosphate solution should be equivalent to less than 0.01 per cent of  $H_2SO_4$ . Although only small quantities of fluorine appear in the ether extracts of superphosphates (Table 10),

TABLE 9.—*Ether-soluble material in commercial superphosphates*  
(Results expressed in percentage of superphosphate sample)

SAMPLE	SUPERPHOSPHATE MADE FROM—	TOTAL	WATER-FREE MATERIAL <sup>a</sup>	H <sub>2</sub> PO <sub>4</sub> <sup>b</sup>	FLUORINE	ORGANIC MATTER, ETC.		FREE WATER	
						BY DIFFERENCE <sup>c</sup>	FOUND <sup>d</sup>	UNCORRECTED RESULT	CORRECTED RESULT
		per cent	per cent	per cent	per cent	per cent	per cent	per cent	per cent
1315	Florida land-pebble phosphate	10.02	3.93	3.77	0.03	0.16	0.16	6.25	-0.19
1316	Tennessee brown-rock phosphate	10.56	5.02	4.85	0.04	0.17	0.17	5.71	-0.21
1338 <sup>f</sup>	Florida land-pebble phosphate	10.71	5.40	5.09	0.02	0.31	0.10	5.62	-0.33
1337 <sup>g</sup>	Florida land-pebble phosphate	5.58	2.20	1.98	0.07	0.22	0.05	3.60	-0.29

<sup>a</sup> Determined by drying the ether residue at 120°C. for 4 hours, and does not include the fluorine.

<sup>b</sup> Exclusive of extracted fluorine.

<sup>c</sup> Water- and fluorine-free material minus H<sub>2</sub>PO<sub>4</sub>.

<sup>d</sup> The ether extract was neutralized by repeated additions of alkali and intervening shaking until the phenolphthalein end point was reached. The ether layer was evaporated to dryness, the small residue treated with a small quantity of water-free ether, and the material thus dissolved was determined gravimetrically. Quantitative recovery could hardly be expected.

<sup>e</sup> Equal to the organic matter (obtained by difference) plus the fluorine.

<sup>f</sup> A small quantity of mineral oil was added during one stage of the manufacture of this material.

<sup>g</sup> Contained no added mineral oil.

they may appreciably affect the results for water. For example, 0.03 per cent of fluorine, if present as hydrofluoric acid, is equivalent to 0.15 per cent of  $H_3PO_4$ ; this would cause the result for weight per cent of extracted acid to be high, and consequently the result for water low, by 0.12 per cent. Results on these superphosphates indicate that a considerable part of the extracted fluorine can be brought into the aqueous solution of the ether-soluble material and included in the titration, if 50 ml. of water is added to the ether extract before the ether is distilled off. On the other hand, if the fluorine is expelled prior to the titration, the error in the result for water will be positive and equal to the quantity of fluorine in the extract. The latter condition, which applies to the data reported herein, is fulfilled, if after the ether has been distilled off, the flask containing the acid residue is gently dried before water is added. A few minutes on the steam bath with a moderate current of air directed into the flask is sufficient. If the fluorine is present as fluosilicic acid, only the details of the relationships would be different. In any event, precision requires uniformity of procedure, and for this reason, if no other, the determination should comply with one or the other of these conditions.

Besides phosphoric acid the ether-soluble material of superphosphate contains organic matter and possibly other substances which, for convenience, will be designated "organic matter." In four samples of superphosphate the quantities of this organic matter, as calculated by difference, ranged from 0.16 to 0.31 per cent of the sample (Table 9). Thus, the results for water determined by the described procedure involve plus errors, which in view of the behavior of phosphoric acid above  $100^\circ C.$ , not to mention the charring of the organic material when the acid residue is dried at  $120^\circ C.$ , must be at least as large as these observed values for organic matter. The figures for free water, when corrected for soluble organic matter and fluorine, give results (Table 9) that are regarded as the closest approach yet possible to the true values for free water in these materials.

As previously indicated, a negative error arises when the extracted fluorine acid is titrated with the phosphoric acid. As this would more or less compensate the positive error due to organic matter, the extracted fluorine should be retained in the solution for titration, unless both corrections are contemplated. On the other hand the extracted acid, etc. may be determined gravimetrically as in Schucht's alcohol method. In routine determinations either course may be adopted, but the former is unquestionably the more convenient one.

#### HYGROSCOPIC WATER

In the light of previous discussion ether extraction is regarded as the most satisfactory method for the determination of hygroscopic water in superphosphate. Although the results on the superphosphates used in this

TABLE 10.—*Fluorine removed from commercial superphosphates in determination of water by several methods*<sup>a</sup>  
(Results expressed in percentage of sample.)

SAMPLE	SUPERPHOSPHATE MADE FROM	FREE ACID <sup>b</sup> AS H <sub>2</sub> PO <sub>4</sub>	TOTAL FLUORINE	FLUORINE REMOVED							EXTRACTION WITH— ABSOLUTE ALCOHOL <sup>g</sup>	ETHER <sup>h</sup>
				IN OVEN AT <sup>d</sup> —			STEAM OF DRY AIR AT 25°C <sup>e</sup>	OTHER CONCENTRATED H <sub>2</sub> SO <sub>4</sub> AT 25°C.		ATMOSPHERIC PRESSURE <sup>f</sup>		
				120°C.	105°C.	80°C.						
Ordinary Superphosphate												
1315	Florida land-pebble phosphate	3.77	1.56	0.43	0.44	0.30	0.16	0.21	0.13	0.00	0.034	
1320	Florida land-pebble phosphate	1.52	1.65	0.52	0.24	0.19	0.00	0.00	0.00	—	0.031	
1316	Tennessee brown-rock phosphate	4.85	1.49	0.31	0.28	0.26	0.04	0.09	0.05	0.00	0.035	
1066	Tennessee brown-rock phosphate	1.93	1.30	0.47	0.21	0.07	0.02	0.00	—	—	0.021	
Double Superphosphate												
1338	Florida land-pebble phosphate	5.09	2.92	0.41	0.39	—	—	—	0.00	0.00	0.039	
1337	Florida land-pebble phosphate	1.98	2.04	0.23	0.24	—	—	—	0.00	0.00	0.069	

<sup>a</sup> The fluorine determinations were kindly made by L. F. Rader, Jr., in accordance with the Willard-Winter method (*Ind. Eng. Chem. Anal. Ed.*, 5, 7 (1933)).

<sup>b</sup> Determined by extraction with ether and does not include extracted fluorine.

<sup>c</sup> Determined by extraction with ether and does not include extracted fluorine.

<sup>d</sup> Dried to constant weight (Table 1).

<sup>e</sup> Dried to constant weight (18 hours).

<sup>f</sup> Dried 48 hours (Table 4).

<sup>g</sup> Dried 3 hours (Table 4).

<sup>h</sup> Determined in the extract.

TABLE 11.—*Water in superphosphates by several methods*  
(Results expressed in percentage of sample.)

SAMPLE	SUPERPHOSPHATE MADE FROM—	WATER					
		FREE ACID <sup>a</sup> AS H <sub>2</sub> PO <sub>4</sub>	IN OVEN AT <sup>b</sup> —			DISTILLA- TION WITH BENZENE	IN STREAM OF DRY AIR AT 25°C. <sup>c</sup>
			120°C.	105°C.	80°C.		
						OVER CONCENTRATED H <sub>2</sub> SO <sub>4</sub> AT 25°C.	EXTRACTION WITH ETHER <sup>d</sup>
						ATMOSPHERIC PRESSURE <sup>e</sup>	ABSOLUTE ALCOHOL
						100 MM. <sup>f</sup>	
Ordinary Superphosphate Prepared Commercially							
1315	Florida land-pebble phosphate	3.77	9.45	8.49	7.50	6.89	6.25
1320	Florida land-pebble phosphate	1.52	7.30	3.57	2.90	1.50	1.29
1316	Tennessee brown-rock phosphate	4.85	9.44	8.41	7.20	6.55	5.71
1066	Tennessee brown-rock phosphate	1.93	9.18	6.85	4.66	2.40	2.27
Ordinary Superphosphate Prepared in the Laboratory							
ES-1A	Tricalcium phosphate, C. P.	1.06	8.96	7.62	3.19	2.69	2.14
ES-1B	Tricalcium phosphate, C. P.	0.46	10.03	8.26	2.94	1.57	1.25
Double Superphosphate Prepared Commercially							
1338	Florida land-pebble phosphate	5.09	11.06	9.14	—	—	5.62
1337	Florida land-pebble phosphate	1.98	6.48	5.73	—	—	3.60

<sup>a</sup> Determined by extraction with ether and does not include extracted fluorine.

<sup>b</sup> Dried to constant weight (Table 1).

<sup>c</sup> Dried to constant weight (18 hours).

<sup>d</sup> Dried 48 hours (Table 4).

<sup>e</sup> Dried 3 hours (Table 4).

<sup>f</sup> Results have not been corrected for fluorine and organic matter.

study leave little choice between the extraction methods (Table 11), it cannot be expected that this good agreement will persist with larger quantities of free water and acid. The results obtained by drying superphosphate over concentrated sulfuric acid under reduced pressure (Table 11) are, on the average, only a little higher than those obtained by ether extraction; and for routine determinations where water only is desired, this rapid and simple method should be satisfactory.

#### WATER OF CRYSTALLIZATION

Monocalcium phosphate monohydrate loses its water of crystallization when it is dried in the oven at 105°C., and incipient decomposition also takes place at this temperature.<sup>1</sup> Under the same conditions calcium sulfate dihydrate retains about 4 per cent of its crystal water (Table 2). However, the loss in weight of acid-free mixtures of these hydrates when they are dried at 105°C. for 24 hours, or at 120°C. for 3 hours, corresponds very closely with the total theoretical water of crystallization of the mixture (Table 2). The relatively large amounts of fluorine that are evolved when superphosphate is dried in the oven (Table 10), can be reduced to 0.12 to 0.30 per cent by removing the free acid and hygroscopic water before the sample is subjected to oven drying. In view of these considerations it would appear that the determination of the crystal water in superphosphate should be made by drying, either at 105°C. for 24 hours or at 120°C. for 3 to 5 hours, the ether-extracted sample from the determination of hygroscopic water.

#### SUMMARY

The principal constituents of superphosphate and of the superphosphate solution are briefly discussed.

The relation between the hygroscopic or free water and the free acid, and also that between the composition of the superphosphate solution and the determination of water are discussed in some detail.

Results are given of an extensive study of several methods for determining water in superphosphate, viz: (1) drying methods, including oven drying and desiccator methods; (2) distillation methods; and (3) extraction methods, in which alcohol or ether is used as an extractant.

The results show (1) that the hygroscopic water in superphosphate can be most satisfactorily determined by the ether-extraction method, which also permits the simultaneous determination of the free acid, and (2) that the water of crystallization can then be determined by drying the ether-extracted sample in the oven at 120°C.

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<sup>1</sup> Stoklass, *Z. anal. Chem.*, 29, 890 (1890).



# PROGRESSIVE CHANGES IN THE COMPOSITION OF EDIBLE SHELL EGGS DURING STORAGE

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A study of the composition of fresh and storage eggs<sup>1</sup> indicates that the differences between these two classes of edible eggs are due to changes produced by osmotic action through the vitelline membrane. The differences are particularly noticeable when the composition of the yolks separated from 2-day-old eggs is compared with that of storage eggs. However, when the value of the various determinations on the whites, yolks, and whole eggs, respectively, are calculated on the basis of the dry substances for the 2-day-old, commercial fresh, and storage eggs, and compared, few or no changes appear, that is other than the transfer of water from the whites to the yolks and the loss of water by evaporation through the shell.

This difference in composition supports the findings of Greenlee,<sup>2</sup> Sharp and Powell,<sup>3</sup> Holst and Almquist,<sup>4</sup> and Romanoff.<sup>5</sup> As the osmotic action is progressive, two experiments were made to ascertain the progress of the changes that occur in both the yolk and white during storage. The results obtained are reported in Tables 1-5.

TABLE 1.—*Number of eggs in sample analyzed, loss due to evaporation, and weight of eggs*

DATE	EGGS IN SAMPLE	LOSS DUE TO EVAPORATION	WEIGHT OF EGGS		
			AVERAGE	MAXIMUM	MINIMUM
		<i>per cent</i>	<i>grams</i>	<i>grams</i>	<i>grams</i>
Cold Storage					
2-17-31	24		57.1	64	50
3-17-31	23		55.7	65	44
4-14-31	24		57.5	68	46
5-12-31	24		55.1	62	46
6- 9-31	24		57.0	67	50
7- 7-31	24		55.5	71	44
8- 4-31	23		55.1	64	46
10-27-31	21		55.5	64	52
11-24-31	24		53.2	62	46
12-22-31	22		53.6	67	44
1-19-32	22		58.2	63	49
4-12-32	23		55.3	62	45
Room Storage					
4- 6-31	24	0.83	54.9	62	49
4-13-31	24	2.91	52.8	68	42
4-20-31	23	5.34	52.9	63	45
4-27-31	23	6.77	50.7	59	44
5- 4-31	22	9.24	49.2	57	43
5-11-31	22	10.75	47.9	57	41

\* A. E. Low, Chief of Station.

<sup>1</sup> *This Journal*, 15, 310 (1932).

<sup>2</sup> U. S. Dept. Agr. Bur. Chem. Cir. 83.

<sup>3</sup> *Ind. Eng. Chem.*, 22, 908 (1930).

<sup>4</sup> *Hälgarda*, 6, 49 (1931).

<sup>5</sup> Cornell Univ. Agr. Exp. Sta. Memoir 132 (1930).

TABLE 2.—*Separation of eggs (per cent)*

DATE	IN WHOLE EGGS				IN EDIBLE PORTION	
	WHITE	YOLK	SHELL	LOSS	WHITE	YOLK
Cold Storage						
2-17-31	58.79	29.69	10.72	0.80	66.45	33.55
3-17-31	57.80	30.58	10.92	0.70	65.40	34.60
4-14-31	57.42	31.50	10.72	0.36	64.58	35.42
5-12-31	57.60	31.07	10.81	0.52	64.96	35.04
6- 9-31	56.36	32.38	11.04	0.22	63.51	36.49
7- 7-31	55.63	33.03	10.81	0.53	62.74	37.26
8- 4-31	54.50	33.49	10.98	1.03	61.94	38.06
10-27-31	53.65	33.82	11.42	1.11	61.37	38.63
11-24-31	53.33	34.14	11.28	1.25	60.97	39.03
12-22-31	53.31	34.66	11.44	0.59	60.60	39.40
1-19-32	52.42	35.78	11.09	0.71	59.43	40.57
4-12-32	51.57	36.32	11.40	0.71	58.71	41.29
Room Storage						
4- 6-31	56.34	31.81	11.24	0.61	63.91	36.09
4-13-31	55.99	31.70	11.75	0.56	63.85	36.15
4-20-31	53.62	34.21	11.76	0.41	61.05	38.95
4-27-31	52.19	35.05	12.34	0.42	59.82	40.18
5- 4-31	50.65	36.14	12.48	0.73	58.36	41.64
5-11-31	50.85	36.05	12.71	0.39	58.52	41.48

TABLE 3.—*Range of room temperature during storage*

DATE	TEMPERATURE
1931	°C.
4-4	24-37
4-5	23-37
4-6 to 4-13	20-28
4-13 to 4-20	24-28
4-20 to 4-27	15-26
4-27 to 5-4	21-26
5-4 to 5-11	14-28

TABLE 4. (Cold Storage). Results on the whites, yolks, and whole egg (per cent)

DATE	SOLIDS	CHLORINE AS NaCl	P <sub>2</sub> O <sub>5</sub>	NITROGEN			FAT (ACID HYDROLYSIS)	DEXTRINE
				TOTAL	WATER-SOLUBLE			
					TOTAL	CRUDE ALBUMIN		
Whites—Original Substance								
2-17-31	12.26	0.27	0.03	1.76	1.63	1.37	0.03	0.32
3-17-31	12.33	0.28	0.04	1.75	1.64	1.38	0.03	0.41
4-14-31	12.22	0.29	0.04	1.73	1.62	1.37	0.03	0.39
5-12-31	12.44	0.30	0.03	1.75	1.65	1.40	0.03	0.37
6- 9-31	12.75	0.29	0.04	1.81	1.69	1.42	0.05	0.40
7- 7-31	12.67	0.29	0.03	1.81	1.67	1.40	0.04	0.33
8- 4-31	13.01	0.30	0.03	1.82	1.72	1.45	0.03	0.41
10-27-31	13.21	0.30	0.03	1.90	1.80	1.54	0.03	0.42
11-24-31	13.56	0.31	0.03	1.93	1.80	1.51	0.03	0.40
12-22-31	13.68	0.31	0.04	1.93	1.85	1.51	0.03	0.41
1-19-32	13.46	0.31	0.04	1.90	1.84	1.51	0.04	0.40
4-12-32	13.62	0.31	0.04	1.92	1.83	1.53	0.03	0.42
Whites—Dry Substance								
2-17-31		2.20	0.24	14.36	13.30	11.17	0.24	2.61
3-17-31		2.27	0.32	14.19	13.30	11.19	0.24	3.32
4-14-31		2.37	0.33	14.16	13.26	11.21	0.25	3.19
5-12-31		2.41	0.24	14.07	13.26	11.25	0.24	2.97
6- 9-31		2.27	0.31	14.20	13.25	11.14	0.39	3.14
7- 7-31		2.29	0.24	14.29	13.18	11.05	0.32	2.60
8- 4-31		2.31	0.23	13.99	13.22	11.15	0.23	3.15
10-27-31		2.27	0.23	14.38	13.68	11.66	0.23	3.18
11-24-31		2.29	0.22	14.23	13.27	11.44	0.22	2.95
12-22-31		2.27	0.29	14.11	13.52	11.04	0.22	3.00
1-19-32		2.38	0.30	14.19	13.74	11.29	0.30	3.05
4-12-32		2.28	0.29	14.10	13.44	11.23	0.22	3.08
Max.		2.41	0.33	14.38	13.74	11.66	0.39	3.32
Min.		2.20	0.22	13.99	13.18	11.04	0.22	2.60
Av.		2.30	0.27	14.20	13.36	11.21	0.26	3.01
Yolks—Original Substance								
2-17-31	51.49	0.31	1.41	2.75	0.55	0.20	32.65	0.17
3-17-31	50.56	0.30	1.42	2.66	0.51	0.18	31.52	0.18
4-14-31	49.83	0.29	1.35	2.70	0.52	0.18	30.89	0.21
5-12-31	48.96	0.28	1.33	2.57	0.50	0.17	30.47	0.18
6- 9-31	48.76	0.29	1.31	2.59	0.53	0.21	30.26	0.21
7- 7-31	48.11	0.29	1.32	2.52	0.54	0.22	29.71	0.19
8- 4-31	47.79	0.28	1.30	2.51	0.52	0.20	29.96	0.19
10-27-31	46.36	0.28	1.27	2.47	0.51	0.21	28.93	0.20
11-24-31	45.96	0.27	1.25	2.44	0.52	0.22	28.26	0.22
12-22-31	45.47	0.27	1.23	2.40	0.54	0.20	28.10	0.22
1-19-32	46.27	0.27	1.26	2.45	0.56	0.20	28.50	0.19
4-12-32	45.86	0.28	1.26	2.36	0.54	0.21	28.15	0.22

## Yolks—Dry Substance

2-17-31	0.60	2.74	5.34	1.07	0.39	63.41	0.33
3-17-31	0.59	2.81	5.26	1.01	0.36	62.34	0.36
4-14-31	0.58	2.71	5.42	1.04	0.36	61.99	0.40
5-12-31	0.57	2.72	5.25	1.02	0.35	62.23	0.38
6- 9-31	0.59	2.69	5.31	1.09	0.43	62.06	0.43
7- 7-31	0.60	2.74	5.24	1.12	0.46	61.75	0.39
8- 4-31	0.59	2.72	5.25	1.09	0.42	62.69	0.40
10-27-31	0.60	2.74	5.33	1.10	0.45	62.40	0.43
11-24-31	0.59	2.72	5.31	1.13	0.48	61.49	0.48
12-22-31	0.59	2.71	5.28	1.19	0.44	61.80	0.48
1-19-32	0.58	2.72	5.29	1.21	0.43	61.59	0.41
4-12-32	0.61	2.75	5.15	1.18	0.46	61.38	0.48
Max.	0.61	2.81	5.42	1.21	0.48	63.41	0.48
Min.	0.57	2.69	5.15	1.01	0.35	61.38	0.33
Av.	0.59	2.73	5.30	1.10	0.42	62.16	0.41

## Whole Egg—Original Substance (calculated from results on whites and yolks)

2-17-31	25.42	0.28	0.49	2.09	1.27	0.98	10.97	0.27
3-17-31	25.56	0.29	0.52	2.06	1.25	0.96	10.92	0.33
4-14-31	25.54	0.29	0.50	2.07	1.23	0.95	10.96	0.32
5-12-31	25.24	0.29	0.49	2.04	1.25	0.97	10.70	0.30
6- 9-31	25.89	0.29	0.50	2.09	1.27	0.98	11.07	0.33
7- 7-31	25.87	0.29	0.51	2.07	1.25	0.96	11.09	0.28
8- 4-31	26.25	0.29	0.51	2.08	1.26	0.97	11.42	0.33
10-27-31	26.04	0.29	0.51	2.12	1.30	1.03	11.19	0.33
11-24-31	26.21	0.29	0.51	2.13	1.30	1.01	11.05	0.33
12-22-31	26.21	0.29	0.51	2.12	1.33	0.99	11.03	0.34
1-19-32	26.77	0.29	0.53	2.12	1.32	0.98	11.59	0.32
4-12-32	26.93	0.30	0.53	2.10	1.30	0.98	11.64	0.34

## Whole Eggs—Dry Substance

2-17-31	1.10	1.93	8.22	5.00	3.86	43.15	1.06
3-17-31	1.13	2.03	8.06	4.89	3.76	42.72	1.29
4-14-31	1.14	1.96	8.10	4.82	3.72	42.91	1.25
5-12-31	1.15	1.94	8.08	4.95	3.84	42.39	1.19
6- 9-31	1.12	1.93	8.07	4.91	3.79	42.76	1.27
7- 7-31	1.12	1.97	8.00	4.83	3.71	42.87	1.08
8- 4-31	1.10	1.94	7.92	4.80	3.70	43.50	1.26
10-27-31	1.11	1.96	8.14	4.99	3.96	42.97	1.27
11-24-31	1.11	1.95	8.13	4.96	3.85	42.16	1.26
12-22-31	1.11	1.95	8.09	5.07	3.78	42.08	1.30
1-19-32	1.08	1.98	7.92	4.93	3.66	43.29	1.20
4-12-32	1.11	1.97	7.80	4.83	3.64	43.22	1.26
Max.	1.15	2.03	8.22	5.07	3.96	43.50	1.30
Min.	1.08	1.93	7.92	4.80	3.64	42.08	1.08
Av.	1.12	1.96	8.07	4.92	3.78	42.80	1.22

TABLE 5. (Room Storage) Results on the Whites, Yolks, and Whole egg (per cent)

DATE	SOLIDS	CHLORINE AS NaCl	P <sub>2</sub> O <sub>5</sub>	NITROGEN			FAT (ACID HYDROLYSIS)	DEXTRIN
				TOTAL	WATER-SOLUBLE			
					TOTAL	CRUDE ALBUMIN		
Whites—Original Substance								
4- 6-31	12.01	0.29	0.03	1.68	1.58	1.34	0.05	0.42
4-13-31	12.93	0.31	0.04	1.82	1.70	1.44	0.04	0.34
4-20-31	13.30	0.32	0.04	1.86	1.74	1.49	0.03	0.41
4-27-31	14.01	0.32	0.05	2.01	1.85	1.55	0.03	0.46
5- 4-31	14.76	0.36	0.04	2.10	1.94	1.64	0.04	0.43
5-11-31	14.95	0.35	0.04	2.12	1.92	1.68	0.03	0.45
Whites—Dry Substance								
4- 6-31		2.41	0.25	13.99	13.16	11.16	0.42	3.50
4-13-31		2.40	0.31	14.08	13.15	11.14	0.31	2.63
4-20-31		2.41	0.30	13.98	13.08	11.20	0.23	3.08
4-27-31		2.28	0.36	14.35	13.20	11.06	0.21	3.28
5- 4-31		2.44	0.27	14.23	13.14	11.11	0.27	2.91
5-11-31		2.34	0.27	14.18	12.84	11.24	0.20	3.01
Max.		2.44	0.36	14.35	13.20	11.20	0.42	3.50
Min.		2.28	0.25	13.98	12.84	11.06	0.21	2.63
Av.		2.38	0.29	14.14	13.10	11.15	0.27	3.07
Yolks—Original Substance								
4- 6-31	50.56	0.30	1.40	2.63	0.50	0.16	31.72	0.17
4-13-31	48.99	0.28	1.33	2.57	0.48	0.16	30.73	0.17
4-20-31	48.72	0.28	1.35	2.53	0.47	0.17	30.81	0.18
4-27-31	48.13	0.27	1.35	2.53	0.43	0.16	29.97	0.19
5- 4-31	48.16	0.29	1.34	2.56	0.46	0.15	29.97	0.19
5-11-31	47.86	0.29	0.31	2.47	0.47	0.15	29.85	0.19
Yolks—Dry Substance								
4- 6-31		0.59	2.77	5.20	0.99	0.32	62.74	0.34
4-13-31		0.57	2.71	5.25	0.98	0.33	62.73	0.37
4-20-31		0.57	2.77	5.19	0.96	0.35	63.24	0.37
4-27-31		0.56	2.80	5.26	0.89	0.33	62.27	0.39
5- 4-31		0.60	2.78	5.32	0.96	0.31	62.23	0.39
5-11-31		0.61	2.74	5.16	0.98	0.31	62.37	0.40
Max.		0.61	2.80	5.32	0.99	0.35	63.24	0.40
Min.		0.56	2.74	5.16	0.89	0.31	62.23	0.34
Av.		0.58	2.76	5.23	0.96	0.33	62.60	0.38
Whole Eggs—Original Substance (calculated from results on whites and yolks)								
4- 6-31	25.92	0.29	0.52	2.02	1.19	0.91	11.48	0.33
4-13-31	25.96	0.30	0.51	2.07	1.26	0.98	11.14	0.28
4-20-31	27.10	0.30	0.55	2.12	1.25	0.98	12.02	0.32
4-27-31	27.72	0.30	0.57	2.22	1.29	0.97	12.06	0.35
5- 4-31	28.67	0.33	0.58	2.29	1.32	1.02	12.50	0.33
5-11-31	28.60	0.32	0.57	2.26	1.32	1.05	12.40	0.34

	Whole Eggs—Dry Substance						
4- 6-31	1.12	2.01	7.79	4.59	3.51	44.29	1.27
4-13-31	1.16	1.96	7.97	4.85	3.77	42.91	1.08
4-20-31	1.11	2.03	7.82	4.61	3.62	44.35	1.18
4-27-31	1.08	2.06	8.01	4.65	3.50	43.51	1.26
5- 4-31	1.15	2.02	7.99	4.60	3.56	43.60	1.15
5-11-31	1.12	1.99	7.90	4.62	3.67	43.36	1.19
Max.	1.16	2.06	8.01	4.85	3.77	44.35	1.27
Min.	1.08	1.96	7.79	4.59	3.50	42.91	1.08
Av.	1.12	2.01	7.91	4.65	3.61	43.67	1.19

### *Experiment 1.—Cold Storage*

A case of infertile eggs, all laid February 18, 1931, was collected from a large commercial flock of single-comb White Leghorns, trucked about 60 miles to Chicago, and left standing overnight at 0°–5°C. Two dozen eggs were then removed as a sample, and the case was placed in the central portion of a large egg room of a commercial cold storage company in Chicago. Samples of eggs were removed periodically for examination. At the end of 35 weeks (October 20, 1931), the case with the remainder of the eggs was wrapped with heavy paper, expressed to St. Louis, and placed in cold storage. During the transfer 4 dozen eggs were broken. Samples of eggs were again removed and examined periodically. Summary: Samples consisting of 2 dozen eggs each were removed and examined at the end of the following weeks of cold storage: 0, 4, 8, 12, 16, 20, 24, 36, 40, 44, 48, and 60, respectively.

### *Experiment 2.—Room Storage*

On April 4, 1931, 144 eggs were collected at Chicago from a consignment of current receipts shipped the previous day from Hamilton, Michigan. The eggs were weighed, 12 at a time, placed into regular retail cartons holding 12 eggs each, and stored on a desk in the laboratory. Samples consisting of 2 dozen eggs each were examined at weekly intervals. The range in temperature on the desk where the eggs were stored April 4 and 5, and thereafter by weeks, is given in Table 3.

The methods used for preparation of the samples and for the analysis were described in a previous paper.<sup>1</sup>

<sup>1</sup> *This Journal*, 15, 310 (1932).

## PREPARATION OF ACETPHENETIDIN FROM *p*-AMINOACETANILID

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Acetphenetidin is prepared either by the acetylation of *p*-phenetidin or by the ethylation of *p*-acetaminophenol. *p*-Phenetidin can be prepared by the reduction of *p*-nitrophenetol, produced by the ethylation of *p*-nitrophenol, or it may be prepared by the reduction of *p*, *p*-diethoxyazobenzene. *p*-Acetaminophenol is prepared by the acetylation of *p*-aminophenol, which is obtained by the reduction of *p*-nitrophenol or *p*-nitrosophenol.

In a recent communication, Haller and Schaffer<sup>1</sup> show that when treated with acetic acid aryl diazonium borofluorides yield acetates of phenols. The method is a general one for the replacement of the amino group by the acetoxy group. As the acetoxy group can be readily replaced by the ethoxy group the two reactions appeared to be useful for the replacement of the amino group by the ethoxy group. This replacement permits the preparation of acetphenetidin from *p*-aminoacetanilid, and as *p*-aminoacetanilid is used in large quantities in the manufacture of dye intermediates and is readily available it seems possible that acetphenetidin can be commercially prepared from it.

In the present investigation the *p*-aminoacetanilid was prepared from U.S.P. acetanilid. Acetanilid was readily nitrated to *p*-nitroacetanilid, which on reduction yielded *p*-aminoacetanilid. This in turn was converted to acetphenetidin, as indicated previously. Acetphenetidin was thus prepared from acetanilid by the following sequence of reactions: Acetanilid→*p*-nitroacetanilid→*p*-aminoacetanilid→*p*-acetaminophenyl diazonium borofluoride→*p*-acetoxyacetanilid→acetphenetidin.

### EXPERIMENTAL PART

*Acetanilid*.—The material used in the experiments to be described was acetanilid, U.S.P. crystals. It melted at 114–115°C. (corr.).

Microscopical examination showed that the habit of the crystals is not significant; when examined with crossed nicols, they showed nothing distinctive, and most of the irregular fragments extinguished sharply. The refractive indices, determined statistically, are as follows:  $n_\alpha = 1.515$ ,  $n_\beta = \text{indeterminate}$ ;  $n_\gamma = > 1.738$  ( $\text{CH}_2\text{I}_2$ ). For determinative purposes, the most commonly occurring refractive index is  $n_1 = 1.620$ .

*p*-Nitroacetanilid.—Acetanilid was nitrated by the following procedure of Nölting and Collin.<sup>2</sup>

<sup>1</sup> *J. Am. Chem. Soc.*, **55**, 4954 (1933).

<sup>2</sup> *Ber.* **17**, 261 (1884).

Fifty grams of acetanilid was dissolved in 200 grams of concentrated sulfuric acid (sp. gr. 1.84) at 20°C. The solution was cooled in an ice salt bath to 0°C., and 29.5 grams of concentrated nitric acid (sp. gr. 1.49) was slowly dropped into the solution, which was constantly stirred with a mechanical stirrer. The temperature was kept between 0 and 5°C. After all the nitric acid had been added, stirring was continued for 1 hour. The solution was carefully poured into 750 grams of cracked ice. The precipitate formed was removed by filtration, thoroughly washed with water, and dried. The yield was 62 grams, 95% of the theory for mono nitroacetanilid. The product was a mixture of *o*-nitro and *p*-nitroacetanilid. The para isomer was separated by the following method of Witt and Utermann.<sup>1</sup>

Fifty grams of the finely powdered nitroacetanilid was slowly added to a solution of 50 cc. of 50% potassium hydroxide, 200 cc. of water, and 50 cc. of ethyl alcohol at 0°C. The mixture was vigorously stirred with a mechanical device for 15 minutes, and then filtered. The residue was washed thoroughly with water until the washings were no longer alkaline to litmus paper. The dried product which was crude *p*-nitroacetanilid weighed 43.5 grams (87%). When recrystallized from 65% alcohol, it melted at 214.5–215.5°C. (corr.).

*Anal.* Calcd. for  $C_8H_8O_2N_2$ : N, 15.55. Found: N, 15.47, 15.54. To identify the product definitely as *p*-nitroacetanilid, a known sample of *p*-nitroaniline was converted into *p*-nitroacetanilid by the method described by Kaufman.<sup>2</sup> The *p*-nitroacetanilid thus obtained melted at 214–215°C. (corr.), and when mixed with an equal quantity of the *p*-nitroacetanilid obtained by nitrating acetanilid no depression of the melting point occurred.

Microscopical examination showed the substance to be colorless and that it crystallizes in fibrous rods. Under crossed nicols, some of the rods extinguished sharply; others remained partly bright when the stage was revolved. According to Arzruni<sup>3</sup> this substance crystallizes in the orthorhombic system, but the findings of the writers indicate that it may crystallize in the monoclinic system as the needles show straight extinction and are elongated parallel to axis-b. The refractive indices as determined statistically are as follows:  $n_\alpha = 1.485$ ;  $n_\gamma > 1.738$  ( $CH_2I_2$ ). An intermediate index,  $n_4 = 1.738$  ( $CH_2I_2$ ) also occurs, but it is not the maximum value.

*p*-Aminoacetanilid.—This compound was readily prepared in quantitative yield on catalytic hydrogenation of *p*-nitroacetanilid. Although this method has not been previously used for the reduction of *p*-nitroacetanilid, it is frequently used for the reduction of nitro groups to amino groups.

Three grams of *p*-nitroacetanilid dissolved in 90 cc. of warm ethyl alcohol was placed in the reaction bottle of a Burgess-Parr catalytic reduction apparatus and 0.2 gram of platinum oxide catalyst<sup>4</sup> was added. The mixture was then shaken in an atmosphere of hydrogen until three molecular equivalents were absorbed. The time required was about 10 minutes. The solution was filtered and concentrated to a small volume under reduced pressure. The product, which crystallized out, was removed by filtration and recrystallized from water. It melted at 164–165°C. (corr.) and when mixed with an equal quantity of authentic *p*-aminoacetanilid, m. p. 164–165°C. (corr.), the melting point was 164.5–165°C. (corr.). On concentration of the filtrate a second crop of the amine was obtained.

Microscopical examination showed this substance to be colorless when first

<sup>1</sup> *Ber.*, **39**, 3901 (1906).

<sup>2</sup> *Ibid.*, **42**, 3480 (1909).

<sup>3</sup> *Z. Krist.*, **1**, 444 (1877).

<sup>4</sup> Adams and Shriner, *J. Am. Chem. Soc.*, **45**, 2171 (1923).



crystallized, but gradually darkening on standing. It consists of rods with square ends. The extinction is straight and the sign of elongation is — when examined with crossed nicols. The double refraction is quite strong. The refractive indices are as follows:  $n_{\alpha} = 1.520$  (lengthwise on rods, and very common);  $n_{\beta} = 1.700$  (also common);  $n_{\gamma} = > 1.738$  ( $\text{CH}_2\text{I}_2$ ).

*p-Aminoacetanilid Hydrochloride*.—This compound was obtained from an alcohol solution of the free base and concentrated hydrochloric acid.

Five grams of *p*-nitroacetanilid was reduced as described above. The alcohol solution was cooled and then filtered into 2.5 cc. of cold concentrated hydrochloric acid. The amine hydrochloride, which soon separated, was removed by filtration, washed with ether, and dried. The yield was 3.6 grams. The filtrate was concentrated under reduced pressure to a small volume, and 100 cc. of dry ether was added. The crystalline precipitate was removed by filtration, washed with an alcohol-ether solution and then dried. The yield was 1.8 grams. The two crops were identical and were combined. Total yield 5.4 grams.

*Anal.* Calcd. for  $\text{C}_8\text{H}_{11}\text{ON}_2\text{Cl} \cdot \text{H}_2\text{O}$ : N, 13.69. Found: N, 13.72, 13.79. The hydrochloride prepared in this manner contained 1 molecule of water. This was lost on heating the hydrate at  $117^\circ\text{C}$ . under reduced pressure.

*Anal.* Calcd. for  $\text{C}_8\text{H}_{11}\text{ON}_2\text{Cl}$  N, 15.01. Found: N, 14.98, 15.19.

When examined microscopically the hydrated material was shown to consist of thin, micaceous plates, more or less six-sided in outline. The plates extinguish sharply with crossed nicols and show striking polarization colors. Statistical determination of the refractive indices gave the following results:  $n_{\alpha} = 1.505$  (common);  $n_{\gamma} = 1.738$  ( $\text{CH}_2\text{I}_2$ ), also common; an intermediate index,  $n_4 = 1.673$ , also frequently occurs, and is useful in determinative work.

*p-Acetaminophenyl Diazonium Borofluoride*.—This compound was readily obtained from *p*-acetaminophenyl diazonium chloride and hydrofluoroboric acid by the general procedure of Balz and Schiemann.<sup>1</sup>

Twenty and four-tenths grams of *p*-aminoacetanilid hydrochloride was added to 12 cc. of concentrated hydrochloric acid and 50 cc. of water. The mixture was cooled to  $0^\circ\text{C}$ . and diazotized by adding slowly through a dropping funnel, with constant mechanical stirring, a solution of 6.9 grams of sodium nitrite in 15 cc. of water; 30 cc. of 40% hydrofluoroboric acid was then added. The *p*-acetoaminophenyl diazonium borofluoride soon separated. It was removed by filtration and washed with alcohol and then with ether. The yield was 20 grams, 84% of the theory. It melted with decomposition at  $135^\circ\text{C}$ . (corr.). When recrystallized from acetone-chloroform solution, the melting point did not change.

*p-Acetoxyacetanilid*.—This compound was obtained by heating *p*-acetaminophenyl diazonium borofluoride in acetic anhydride until all the nitrogen was eliminated.

Twelve and five-tenths grams of *p*-acetaminophenyl diazonium borofluoride in 65 cc. of acetic anhydride was heated under reflux until nitrogen was no longer given off. On cooling the reddish brown solution, a crystalline product was deposited. It was removed by filtration, washed with acetic anhydride, then with benzene, and dried. It contained boron and fluorine. It is probably a coordination compound of *p*-acetoxyacetanilid and boron trifluoride. On recrystallization from water a product

<sup>1</sup> *Ber.*, 60, 1186 (1927).

free from boron and fluorine was obtained. The yield was 3 grams. It melted at 151.5–152.5°C. (corr.).

*Anal.* Calcd. for  $C_{10}H_{11}O_3N$ ; N, 7.25. Found: N, 7.23, 7.23.

The acetic anhydride filtrate was concentrated under reduced pressure to a small volume. Water was added, and the solution was neutralized with solid sodium carbonate. The separated oil was extracted with ether. The ether extract was washed with water and dried over sodium sulfate. After removal of the ether 2 grams of *p*-acetoxyacetanilid was obtained. The combined yield of *p*-acetoxyacetanilid obtained was 5 grams. Yield, 51.5% theory.

A comparison of the optical properties of the compound obtained in the reaction described above with those of *p*-acetoxyacetanilid which was obtained on acetylation of *p*-aminophenol showed them to be identical. The melting point of equal parts of the two compounds was 151.5–152.5° (corr.).

The *p*-acetoxyacetanilid obtained in the reaction described above sometimes had a melting point of about 113°C. (uncorr.). The optical properties were the same as those of the product melting at 151.5–152.5°C. (corr.). Furthermore, it was readily converted to acetphenetidin (for procedure see below). On sublimation the compound melted at 151.5–152.5°C. (corr.).

Microscopical examination showed that this substance is colorless and consists of thin, micaceous plates. These plates extinguish sharply with crossed nicols. The refractive indices determined statistically are as follows:  $n_\alpha = 1.510$  (very common):  $n_\beta = \text{indeterminate}$ :  $n_\gamma = > 1.738$  ( $\text{CH}_2\text{I}_2$ ). An intermediate index,  $n_1 = 1.570$ , is also commonly found on the finely powdered material.

*Acetphenetidin (p-Ethoxyacetanilid).*—This compound was obtained on treating *p*-acetoxyacetanilid with ethyl iodide and sodium ethylate. While this particular reaction has not been carried out before, the procedure is a general one for the introduction of an alkyl group.

To 0.46 gram of sodium in 35 cc. of absolute ethyl alcohol were added 4 grams of *p*-acetoxyacetanilid and 6.25 grams of ethyl iodide. The solution was refluxed for 30 minutes; 50 cc. of hot water was then added. On cooling, a crystalline product separated. It was removed by filtration and dried. Yield, 2.0 grams. The filtrate was concentrated under reduced pressure to about one-fourth its volume, and a second crop of crystals was then obtained. These were removed by filtration and dried. Yield, 1.5 grams. Total yield, 3.5 grams, 97% theory. The product was recrystallized from 10% alcohol. It melted at 134–135°C. (corr.). When mixed with an equal quantity of acetphenetidin there was no depression of the melting point.

When examined microscopically the substance<sup>1</sup> is shown to be colorless and to consist of irregular fragments when crushed for examination by the optical immersion method. Some of the fragments extinguish sharply with crossed nicols, while others remain essentially bright under the same conditions. When examined in convergent polarized light (crossed nicols), such fragments show a biaxial interference figure with one optic axis in the microscopical field. The refractive indices are as follows:  $n_\alpha = 1.512$ ;  $n_\beta = 1.574$ ;  $n_\gamma = > 1.738$  ( $\text{CH}_2\text{I}_2$ ). The intermediate value is the most frequently found and diagnostic for the substance. According to Groth<sup>2</sup> acetphenetidin crystallizes in the monoclinic prismatic system, with  $2V = 62^\circ 14'$ .

## SUMMARY

Acetphenetidin was prepared from acetanilid by the following sequence

<sup>1</sup> Fischer and Kofler, *Arch. Pharm.*, **270**, 433–435 (1932), Haas, *Emich Festschrift (Mikrochemie)*, pp. 88–119 (1930).

<sup>2</sup> *Chem. Kryst.*, **4**, 242 (1917).

of reactions: Acetanilid→*p*-nitroacetanilid→*p*-aminoacetanilid→*p*-acetaminophenyl diazonium borofluoride→*p*-acetoxyacetanilid→acetphenetidin.

The optical-crystallographic properties of acetanilid and the compounds obtained in the transformations are given. They were determined by the immersion method.

## SOME OBSERVATIONS ON THE USE OF AUTOMATIC EXTRACTORS

By L. E. WARREN (U. S. Food and Drug Administration,  
Washington, D. C.)

Several years ago Palkin, Murray and Watkins,<sup>1</sup> and somewhat later Palkin and Watkins,<sup>2</sup> developed several forms of automatic apparatus for the assay of galenical preparations and crude drugs.\* One of the two principal types described was for solvents lighter than water, and the other was for heavier solvents.

As the greater part of the writer's observations has been made with the type of extractor using solvents heavier than water, this paper deals more particularly with that form. The criticisms will be considered first.

### CRITICISMS

*Lack of capacity.*—If made according to the specifications of Palkin, Murray and Watkins, the inner tube holds only about 100 cc. and a safe working capacity is about 80 cc. An excess of these limits is particularly likely to occur in drug assays when ether-chloroform solutions are shaken out with diluted sulfuric acid to remove alkaloids. If the aqueous-acid solution exceeds the working capacity of the extractor, it will flow over into the solvent reservoir, and so ruin the assay. The alternatives are to reduce the volume by evaporation before placing the mixture in the extractor or to employ hand separators of suitable size. The problem was solved by the writer by designing extractors of larger capacities (for small quantities of liquid a smaller instrument was made) by increasing the distance from the bottom of the jacket to the delivery tube and by increasing the length and diameter of the jackets, and correspondingly, the size of the inner tubes. The dimensions of the "spider" tubes were increased throughout—the diameter of the spider head from approximately 2.0 cm. to about 3.0 cm. and the number of openings from 12 to 16 to 30 or 32. If the analyst uses several sizes of extractors it is convenient to have an identification mark etched on the jacket and a corresponding mark on the

<sup>1</sup> *Ind. Eng. Chem.*, 17, 612 (1925).

<sup>2</sup> *Ibid.*, 19, 535 (1927); *J. Am. Pharm. Assoc.*, 16, 1039 (1927).

\* For the assay of crude drugs Palkin and Watkins employed a form of extractor (Type S) in which the solvent percolated upward through the drug. This type of extractor may be used also for extracting powdered tablet material.

TABLE 1.—Specifications for automatic extractors of different capacities

EXTRACTOR	JACKET*	INNER TUBE		OPERATING CAPACITY		SOLVENT REQUIRED FOR CHARGING		RESIDUAL SOLVENT	
		cm.	cm.	cc.	cc.	CHLOROFORM	BENZOL	CHLOROFORM	BENZOL
A	28	24	24						
	13								
	3	2	1½†	40	35	100	50	20	10
B	32	28	28						
	13								
	4	3	2†	80	100	125	100	50	10
C	33	29	29						
	15								
	4	3	2½†	100	125	150	125	50	10
D	34	29	29						
	17								
	4	3	3†	150	150	180	175	60	25
E	40	36	34						
	20								
	4	3	3†	200	150	200	200	60	30
F	42	37	37						
	24								
	4½	3½	3†	250	200	200	200	60	30
G	42	37	37						
	25								
	6½	5	3†	500	500	500	200	200	30

\* The dimensions are given in the following order: length, delivery (distance from bottom), diameter.

† Diameter of spider head.

inner tube. The working capacity may also be stated. In choosing an extractor for a particular analysis it is well to select one a size or two larger than is believed to be needed and thereby allow for expansion in volume due to washings, tests for complete extraction, necessary changes in reactions, etc.

The approximate dimensions for several convenient sizes of extractors are given in Table 1, as are the approximate working capacities of the respective instruments, the quantities of solvent required for the initial charge, and the approximate quantities of solvent remaining in the instrument after it has been tilted.

Examination of Table 1 shows that the length and diameters of several of the instruments differ very little. Variations in capacity occurred when the distances of the side delivery tube from the bottom were increased.

*Fragility.*—The jackets were formerly extremely liable to break at the junction of the side delivery tube with the main body of the instrument, but this objection was overcome by making the apparatus of Pyrex. If the jacket is held by the side delivery tube when the apparatus is charged considerable strain occurs at the junction. With Pyrex, however, the liability of breakage in this manner is not great unless the apparatus is one of the larger sizes, in which case it should be provided with some form of support when in use. It should not be carried by the side delivery tube when charged.

*Quantity of solvent required.*—It has been claimed that the extractors require a larger amount of solvent than the hand-shaking procedure. This is a valid objection, but it may be overcome to a considerable extent by a suitable system of recovery of the solvent by distillation.

*Paucity of directions.*—No directions were given in the original paper for testing for complete extraction of the material. At the completion of the extraction the directions were that the solvent in the jacket be separated from the aqueous liquid and added to the main portion. This requires transfer of the liquids to a separator. If extraction is not complete, the liquids must be placed in a clean extractor or the operation must be completed in a hand separator. Presumably the tests for complete extraction were intended to be made at this stage. The writer tilts the extractor backward in such a manner that the reservoir of solvent may be removed without loss. The extractor is then tilted in the opposite direction, and the overflowing solvent is collected in a clean beaker. The solvent is evaporated and the residue subjected to suitable tests. If extraction is not complete, a fresh reservoir of solvent is attached to the apparatus and the extraction is continued.

#### ADVANTAGES

*Time element.*—The writer has made numerous comparisons of this feature, using a cumulator for recording the time actually used by the analyst

in each operation, and has found that in the analysis of galenicals that do not ordinarily give troublous emulsions there is a saving in time of from 10 to 30 per cent. In preparations that tend to form emulsions the saving in time is much greater than this, and in some instances it is so great that the extractor method is shown to be practicable and workable and the

TABLE 2.—*Analyst's time required for the assay of preparations of various types*

PREPARATION		U.S.P. X METHOD	HAND SHAKE OUT (OTHER THAN U.S.P.)	AUTOMATIC EXTRACTOR	TIME GAINED OR LOST BY USE OF AUTOMATIC EXTRACTOR
		minutes	minutes (U.S.P.XI)	minutes	per cent
Tincture cinchona compound	I	98	85	65	+50.8
					+30.8
Tincture cinchona	I	90	85	80	+12.0
	II	99		91	+8.0
Caffeine citrated	I	49		40	+18.0
	II	42		34	+18.0
Chocolate emulsion of quinine sulfate			Unworkable	Chloroform 146	+100.0
				Ether 94	+100.0
			Unworkable		
500 cc. containing 0.5120 gram of anhydrous quinine			112	82	+26.9
Emulsion of liquid petro- lum	(Röhrig tube) 59			Hartmann extractor 55	+7.2
Cyclobarbitol tablets			A.O.A.C. method for barbitol 72	38 33	+47.0 +54.0
Barbital tablets			A.O.A.C. method 64	Warren automatic percolator 49	+30.6
Fluidextract nux vomica			(N.F.V. Method) 64	72 70	-12.0 -9.0
Quinine sulfate tablets			131	91	+30.0
Amidopyrine-phenobarbital mixture			108	91	+15.7
			110	105	+4.6

other to be impracticable or even impossible. Also, some substances that are very soluble in water may be extracted from their aqueous solutions with a great saving in time. For example, citric and lactic acids (both very soluble in water) may be removed quantitatively from their aqueous solutions by ether,<sup>1</sup> but to shake out such solutions by hand would be extremely tedious. The results of several comparative analyses are given in Table 2.

In any comparisons of the two methods with respect to economy of time the difference between the *elapsed time* and the *analyst's time* must be considered. Owing to the greater duration required for the extraction of active principles by the automatic extractor (as compared with the hand extractor) the *total elapsed time* required for a given analysis will usually be greater if the automatic apparatus be used. This feature should be considered when the release of goods is urgent or the time permitted for an analysis is limited.

*Adaptability to emulsions.*—Usually emulsions are analyzed in a Mojonier<sup>2</sup> fat extractor or by the Roese-Gottlieb method<sup>3</sup> in a Röhrig-Biesterfeld<sup>4</sup> tube. The writer has used the Type B automatic extractor, but has found no marked advantages in its use over the methods mentioned above except some saving in time.

In the assay of alkaloid-bearing galenicals the writer has encountered emulsions which had been formed in hand separators and which no form of treatment except evaporation in an acid medium would break up. When such emulsions were placed on the chloroform layer in the automatic extractor and extracted with chloroform, all the alkaloid would be removed in four or five hours without any apparent change in the condition of the emulsion. Complete extraction was proved by destruction of a portion of the emulsion by heating it with dilute hydrochloric acid and further extraction with chloroform after again making alkaline.

*Adaptability to tablets.*—If the tablet being analyzed is soluble in water, it is dissolved in that solvent, the solution is placed in the extractor previously charged with a suitable solvent, and the active principle is extracted in the usual way. If chloroform is to be used for water-insoluble materials, it will be found helpful to plug the lower end of the inner tube with cotton before charging the apparatus to collect any solid particles which otherwise might fall to the bottom and be carried over into the reservoir.

The automatic extractor is useful in the assay of preparations containing barbital or related compounds, most of which are in the form of tablets. Others are on the market, chiefly as sodium compounds dissolved in elixirs or other sweetened liquids, and a few contain the sedative dissolved

<sup>1</sup> *This Journal*, 16, 435, (1932).

<sup>2</sup> U. S. Patent No. 1,255,329, also No. 1,390,308.

<sup>3</sup> Röhrig, A., *Z. Nahr. Genussm.*, 9, 531 (1905).

<sup>4</sup> Biesterfeld, and Evanson, *J. Ind. Eng. Chem.*, 9, 1111 (1917).

in alcohol, glycerin and water. The active principle may be removed readily from such preparations by chloroform or ether. The finely powdered tablet material is suspended in acidified water and extracted with chloroform. The solutions, elixirs, etc., are made very slightly alkaline with sodium hydroxide, diluted with water, and evaporated to the original volume to remove alcohol. They are again diluted with water, acidified with diluted sulfuric acid, and extracted with chloroform or ether. The solvent is washed and evaporated, and the residue is weighed. If the preparation is sweetened with soluble saccharin, this synthetic will appear with the barbital derivative, and a determination of organic sulfur in the extracted material is necessary.

Some types of crude drugs may also be extracted in the automatic extractor. By using as a percolator an inner tube that has been sealed off at the bottom and provided with perforations to allow the percolate to escape, it is possible to exhaust the drug with any of the usual solvents. In packing the percolator in determining the alcohol-extract of crude drugs it is convenient to place a wad of cotton at the bottom to act as a filter. Also drugs which are to be assayed for resins, such as ipomea, jalap, podophyllum or compound jalap powder, may be exhausted with alcohol in this apparatus. However, in general, the automatic extractor possesses no advantages for this type of work over the automatic percolator described by the writer before this Association two years ago.<sup>1</sup>

*Adaptability to Headache Remedies:* The automatic extractor is useful in the analysis of certain types of headache remedies which contain more than one ingredient. Preparations containing caffeine and acetanilid or caffeine and acetphenetidin are finely powdered and suspended in water in the inner tube of the extractor. An acid reaction is insured by the addition (if necessary) of sufficient diluted acetic acid. The organic medicinal substance is then removed by chloroform in the usual way. The chloroform is washed and evaporated, and the residue is hydrolyzed according to the A.O.A.C. procedure. The aqueous-acid solution is placed in an automatic extractor, and the caffeine is removed by chloroform. Finely powdered sodium bicarbonate is then added through a funnel to the contents of the inner tube in portions of about 0.2 gram each until the solution becomes faintly alkaline to litmus paper. A few drops of acetic anhydride are added, and the regenerated acetanilid (or acetphenetidin) is removed by chloroform.

A mixture consisting of 5 grams of amidopyrine and 0.5 gram of phenobarbital was prepared, and portions were treated by dissolving in 5 per cent sodium hydroxide and extracting with chloroform in the Palkin, Murray, Watkins apparatus. The chloroform was washed with water containing a trace of sodium hydroxide, the solvent was evaporated, and the residue

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<sup>1</sup> *This Journal*, 15, 629 (1922).



was dried at 80° and weighed as amidopyrine. After the removal of amidopyrine, the alkaline solution in the extractor was acidified with dilute sulfuric acid and the solution was extracted with chloroform. The solvent was washed with water slightly acidified with hydrochloric acid and evaporated. The residue was dried at 100° and weighed as phenobarbital. The results of a single analysis are given in Table 4.

TABLE 4.—*Separation of amidopyrine and phenobarbital*

INGREDIENT	COMPOSITION OF MIXTURE	FOUND	RECOVERY
	per cent	per cent	per cent
Amidopyrine	90.91	91.37	100.50
		90.43	99.48
		90.64	99.70
Phenobarbital	9.09	9.16	100.80
		8.71	95.82
		8.54	93.95

## SUMMARY

The advantages of the automatic extractor, as compared with the hand separator, outnumber the disadvantages and even surpass them in their importance. The apparatus is not satisfactory for mixtures of solvents unless the boiling points of the constituents are similar. It may be made in several sizes. If made of Pyrex it is very durable. By the use of the automatic extractor in the more usual analyses from 10 to 20 per cent of the analyst's time may be saved. In more difficult separations, particularly those readily producing emulsions, the saving is greater. Many pharmaceuticals, such as elixirs, emulsions, fluidextracts, powders, solutions, suspensions, sirups, tablets and tinctures, may be assayed with greater facility than they can be by the hand separator. Also certain organic acids may be separated from their compounds in mixtures and obtained in a free state more easily than they can be by other means.

*Acknowledgment.*—The writer wishes to thank W. B. Symonds of the Bureau of Chemistry and Soils for making the automatic extraction apparatus in the several sizes.

## ACID CONSTITUENTS OF FOOD PRODUCTS

SPECIAL REFERENCE TO CITRIC, MALIC,  
AND TARTARIC ACIDS

By B. G. HARTMANN and F. HILLIG (Food Control,\* U. S. Department of Agriculture, Food and Drug Administration, Washington, D. C.)

During several years the writers have examined a large number of food products for their citric, malic, and tartaric acid content for the purpose

\* W. B. White, Chief.

of obtaining data that might prove helpful in the interpretation of food analysis. Citric and malic acids occur as normal ingredients in practically all the materials examined. Tartaric acid is not a commonly occurring plant acid; it has been definitely identified only in the grape and the tamarind.

Other fruit acids that have been reported in the literature are oxalic, lactic, salicylic, succinic, quinic, glyoxylic, benzoic, and isocitric acids, tannins, and pectins. Although not acids in a strict sense, tannins and pectins behave like acids in that they are precipitable with lead acetate and are partially titratable with alkali.

#### LITERATURE

Arbenz (1) reported the presence of oxalic acid in the raspberry, currant, orange, grape, pear, prune, and the apple. Of 53 food products examined by Widmark and Ahldin (2), 35 contained oxalic acid. Of the common vegetables, spinach showed 0.84, parsley, 0.24, and rhubarb 0.41 per cent; sorrel contained 2.26, tea 1.39, cocoa 0.65, and roasted coffee 0.04 per cent total oxalic acid. Franzen and his co-workers (3) detected lactic acid in the apple, raspberry, cherry, and the tamarind. Traphagen and Burke (4) found salicylic acid in the strawberry, raspberry, blackberry, apricot, crabapple, orange, currant (5.7 mg. per 100 grams), plum (2.8), cherry (4.0), apple (2.4), and the Concord grape (3.2 mg.). Franzen and Ostertag (5) identified succinic acid in the grape (*vitis vinifera*), rhubarb, raspberry, and the cherry, and Nelson (6) found this acid in the blackberry. Kohman and Sanborn (7) isolated quinic acid from the cranberry and prune, and Semichon and Flanzky (8) found glyoxylic acid in grape juice. Benzoic acid has been determined in the cranberry, and Nelson (9) discovered isocitric acid in the blackberry.

The literature contains little reliable information on the acid constituents of vegetables. Nelson and Mottern (10) reported citric, malic, and oxalic acids in broccoli, spinach, and lettuce. Arbenz (1) reported oxalic acid in the potato, bean, spinach, beet, tomato, cauliflower, onion, mushroom, and in celery root.

The references cited represent only a small part of the published data, but considered in the light of present knowledge of analytical procedure, it is believed that they are reliable.

Extensive work has been done on the identification of the acids of plants. Wehmer (11) cites 115 references on the entire plant of the grape, one-half of which deal with acids. Several of the references date back to 1830, and one by Scheele, on the identification of tartaric acid, is given as 1769.

Nelson (12) has identified the principal acid constituents of many fruits by the Franzen esterification method (13), which is the most reliable chemical method for identifying organic acids. The results obtained

by Nelson and by the writers on nine of the more common fruits follow. Although the samples used were not the same, the data for malic and citric acid are similar.

FRUIT	MALIC ACID		CITRIC ACID		RATIO, CITRIC:MALIC	
	NELSON	HARTMANN-HILLIG	NELSON	HARTMANN-HILLIG	NELSON	HARTMANN-HILLIG
	<i>per cent</i>	<i>per cent</i>	<i>per cent</i>	<i>per cent</i>		
Cranberry	0.46	0.49	1.82	1.59	4:1	3:1
Currant	0.05	0.13	2.30	1.92	46:1	15:1
Loganberry	0.08	0.33	2.02	1.82	25:1	6:1
Pear	0.12	0.16	0.24	0.42	2:1	3:1
Pineapple	0.12	0.12	0.84	0.77	7:1	6:1
Quince	0.68	1.59	None	None		
Raspberry (black)	None	0.05	1.06	0.81		16:1
Raspberry (red)	0.04	0.05	1.30	1.28	33:1	26:1
Strawberry	0.10	0.16	0.91	1.08	9:1	7:1

Nelson and Mottern (14) examined the barley, maize, rye, wheat, and oat plant by the Franzen procedure and found malic, citric, oxalic, and aconitic acids in all these grasses; malonic acid in barley, oats, and wheat; and tricarballic acid in barley and maize. Turner and Hartman (15) reported citric, malic, and malonic acids in alfalfa.

#### ANALYTICAL METHODS

The acid-potassium-tartrate and the Kling procedures are used most generally for determining the total tartaric acid content of food products.

An historical sketch of the tartrate method, published by Hartmann, Eoff and Ingle (16), states that in the presence of free tartaric acid the Halenke-Möslinger wine method (17) gives low results. Hartmann and Eoff modified this method by neutralizing the acidity of the wine with alkali and adding the molecular equivalent of tartaric acid, thereby avoiding the formation of hydrochloric acid. The procedure was officially adopted for wines by the Association of Official Agricultural Chemists (18). However, it was found that the method gives high results when applied to fruit products, such as jams and jellies, because acid-reacting substances other than cream of tartar are occluded in the tartrate precipitate. The writers devised a procedure for fruit products differing from the wine method in that the acid is separated from sugars by precipitation with lead acetate. It has been found suitable for food control work and was tentatively adopted by the A.O.A.C. (19). This method was used in obtaining the tartaric acid data recorded in this paper.

The Kling procedure (20) for the determination of total tartaric acid in fruit products was studied collaboratively by Nelson (21), and as a result the method was adopted tentatively by the A.O.A.C. (22). Later

Hartmann and Hillig investigated the method (23) and found that by removing the pectin and isolating the acid as the lead salt, a cleaner precipitation of calcium racemate is obtained. Both methods are equally accurate, but the tartrate method is more satisfactory for control work because it is less time-consuming and does not require the use of the expensive 1-ammonium-tartrate reagent.

In 1895 Stahre published his discovery of the conversion of citric acid into pentabromacetone (24). Kunz, elaborating on the Stahre reaction, published a procedure for the quantitative determination of citric acid (25). Dunbar and Lepper (26) conducted a collaborative study of the Kunz procedure and showed that with quantities of not less than 50 mg. the acid can be satisfactorily determined. As a consequence, the procedure was adopted tentatively by the A.O.A.C. (27). The writers (28) investigated the various phases of the Kunz method and devised a satisfactory procedure for food control work (29), which was adopted tentatively by the A.O.A.C. (30) and was therefore used in the citric acid work here recorded.

Clifford (31) found that in the determination of citric acid in coffee the precipitated pentabromacetone is contaminated with large quantities of alcohol-ether-soluble material. He overcame this difficulty by subjecting the pentabromacetone precipitate to sublimation instead of treating it with alcohol-ether. The modification also makes possible the identification of the sublimed pentabromacetone through a melting-point determination. The writers have found that when the sample contains an appreciable quantity of proteinaceous material the Clifford procedure is advisable.

There is no known specific precipitant for malic acid. Nelson studied the conversion of malic acid to racemic acid by the fumaric acid route (32). He reported satisfactory results on pure solutions, but not in admixture with other acids and sugars; moreover, the conversion is too intricate and time-consuming to warrant its use in food control work.

Bacon and Dunbar described a method based upon the polarimetric properties of the uranium-malic acid complex (33). Bigelow and Dunbar (34) applied the method to a large number of fruits, principally apples, cherries, and pears. They stated that in the examination of colored fruits "much difficulty is sometimes encountered in making the polarizations and it is then necessary to resort to the use of bromine as a bleaching agent." This treatment removes color, but it affects the accuracy of the method. Nevertheless, the results of these pioneer workers compare favorably with those obtained in recent investigations.

By elaborating Bacon and Dunbar's work the writers devised a serviceable method for food control purposes (35), and used it to obtain the malic acid results recorded in the tables. The malic acid is isolated by means of lead acetate and tribasic lead acetate and then determined by the optical rotation of the uranium complex.

At present no reliable methods for the quantitative determination of some of the acids occurring in fruits are available. Although the procedure developed by Franzen and his coworkers is reliable for the identification of the acid constituents of plants, the large quantities of material required make its general application in food control analysis impracticable, if not prohibitory.

The method of Arbenz (1) for oxalic acid seems reliable, but it is questioned whether in all cases the oxalic acid determined is contained in the plant as such, because under certain conditions vitamin C (36) and glyoxylic acid split off oxalic acid.

The A.O.A.C. methods for the identification and determination of benzoic acid (37) have been found satisfactory for general food work; however, in some cases, particularly with small quantities of the acid, sublimation is recommended. Even sublimation, as Monier-Williams has shown, "may fail if any considerable amount of impurity is present." After studying the methods for determining benzoic acid this investigator devised a procedure (38) for food products that gives excellent results. Hortvet described a sublimator (39) which has been found valuable in food control laboratories.

A quantitative method is needed for the determination of isocitric acid in fruit products. The acid is optically active, and because of the structural arrangement of its molecule it does not form pentabromacetone, characteristics that definitely differentiate it from its isomer, citric acid. Isocitric acid has only been identified in the blackberry. It is interesting to note that in the examination of the loganberry, which is believed by some to be a cross between the blackberry and the raspberry, Nelson (40) did not detect isocitric acid.

There is no reliable method for the quantitative determination of lactic acid in fruit products. Bacon and Dunbar (41) studied the conversion of the acid to oxalic acid in alkaline permanganate oxidation, Kunz (42) separated the acid as the barium salt, and Nelson (43) modified the Kunz procedure and applied the Phelps-Palmer method (44).

The aldehyde procedure, which has found recognition in biochemistry, is not suitable for general food control work. The method titrates the aldehyde that is formed through the oxidation of the acid with permanganate. Friedmann and Graesser (45), in discussing the technic of the method, state that "it was found that the oxidation to aldehyde appears to depend upon factors such as the concentration of oxidation agent added, the acidity of the solution, the concentration of the  $\text{MnSO}_4$  and probably also the amount of lactic acid oxidized."

F. L. Hart of this Department, in an investigation of the chemical composition of commercial milk powders (unpublished), studied the aldehyde procedure. From the poor results obtained he concluded that in its present form this method is not suitable for the examination of milk in food

control work. Fuchs (46) recently described an apparatus for the oxidation of lactic acid, for which he claims 100 per cent efficiency. He emphasizes the fact that the permanganate must be added slowly and uniformly in order to prevent *further* oxidation of the aldehyde formed. Hartmann and Hillig (47) applied the oxalic acid procedure to the determination of lactic acid in milk and milk products. Semichon and Flanzky (48) described a procedure for the determination of lactic acid based upon its oxidation to acetic acid. They also reported a procedure for the determination of succinic acid in wines and fermented liquids (49) that is based upon a chromic oxidation in which other acids are oxidized without affecting the succinic acid.

TABLE 1.—*Malic and citric acid content of fruits*

FRUIT	MALIC ACID	CITRIC ACID	ACIDITY IN TERMS OF PREDOMINATING ACID	
			TITRATABLE	DETERMINED
	<i>per cent</i>	<i>per cent</i>	<i>per cent</i>	<i>per cent</i>
Apples				
Crab	1.02	0.03	0.82	1.05
Delicious	0.27	None	0.18	0.27
Grimes Golden	0.72	None	0.50	0.72
Jonathan	0.75	None	0.51	0.75
McIntosh	0.72	None	0.54	0.72
Rome Beauty	0.78	None	0.56	0.78
Yellow Transparent	0.97	0.02*	0.83	0.99
Apricot, canned	0.33	1.06	0.96	1.37
Banana	0.50	0.15	0.27	0.66
Banana	0.37	0.32	0.28	0.71
Cherry, Montmorency, canned	1.45	None	1.06	1.45
Cranberry	0.49	1.59	2.48	2.06
Currant, canned	0.13	1.92	1.87	2.04
Grape Fruit	0.08	1.33	1.16	1.41
Grape Juice, Concord†	0.31	0.02	1.15	1.44
Lemon Juice	0.29	6.08	6.20	6.36
Loganberry, canned	0.33	1.82	2.08	2.13
Orange, Florida	0.18	0.92	0.80	1.09
Pear, Bartlett, canned	0.16	0.42	0.39	0.57
Peach, Palora, canned	0.69	0.05	0.46	0.74
Pineapple	0.12	0.77	0.79	0.88
Plum, California	0.92	0.03	0.62	0.95
Plum, Damson	2.48	None	2.20	2.48
Prune, Italian Style	1.44	None	1.12	1.44
Quince	1.59	None	1.26	1.59
Raspberry, Black, canned	0.05	0.81	0.78	0.86
Raspberry, Red, canned	0.05	1.28	1.16	1.33
Strawberry, Everbearing	0.16	1.08	1.02	1.23
Youngberry, canned	0.24	0.62	1.05	0.85

\* Triplicate determinations.

† Tartaric acid, 1.07 per cent.

Hartmann and Hillig (50) devised a procedure for the determination of synthetic (inactive) malic acid. This acid is now in use as an acidulent in the preparation of fruit products. It is produced by the catalytic oxidation of benzene to maleic acid and the conversion of the latter into malic acid by heating with water under pressure.

## ANALYTICAL DATA

Wherever possible, fresh sound fruit was used for the determinations. The exceptions are noted in Table 1. The canned fruits consisted of water packs. The data are calculated to original fruit. The vegetables (Table 2) were the usual commodities sold in the market. Only the edible portion of the materials was used. The sample solution was obtained by boiling 300

TABLE 2.—*Malic and citric acid content of vegetables*

VEGETABLE	MALIC ACID	CITRIC ACID	ACIDITY IN TERMS OF PREDOMINATING ACID	
			TITRATABLE	DETERMINED
	per cent	per cent	per cent	per cent
Artichoke	0.17	0.10	0.54	0.26
Asparagus	0.10	0.11	0.27	0.22
Avocado	None	None	12 cc*	—
Beets	None	0.11	0.17	0.11
Beans, Lima	0.17	0.65	0.21	0.81
Beans, String, green	0.13	0.03	0.12	0.16
Broccoli	0.12	0.21	0.43	0.32
Brussels Sprouts	0.20	0.24	0.33	0.43
Cabbage	0.10	0.14	0.15	0.24
Carrot	0.24	0.09	0.08	0.33
Cauliflower	0.39	0.21	0.22	0.61
Celery	0.17	0.01	0.11	0.18
Corn, Sweet	None	None	19.3cc*	—
Cucumber	0.24	0.01	0.07	0.25
Eggplant	0.17	None	0.13	0.17
Kale	0.05	0.35	0.23	0.40
Lettuce, Head	0.17	0.02	0.10	0.19
Mushroom	0.14	None	0.21	0.14
Okra	0.12	0.02	0.14	0.14
Onion	0.17	0.02	0.18	0.19
Parsnip	0.35	0.13	0.17	0.49
Peas, fresh from pod	0.08	0.11	0.16	0.19
Potato, White (Idaho)	None	0.51	0.30	0.51
Potato, Sweet (Cuban)	None	0.07	0.53	0.07
Pumpkin	0.15	None	0.03	0.15
Squash	0.32	0.04	0.08	0.36
Spinach	0.09	0.08	0.17	0.17
Tomato	0.05	0.47	0.47	0.52
Turnip, White	0.23	None	0.10	0.23

\* 0.1 normal acid per 100 grams.

TABLE 3.—*Citric acid, miscellaneous foods*

ITEM NO.	PRODUCT	CITRIC ACID
		per cent
1	Oyster, Chesapeake Bay, meat	0.04
2	Oyster, Chesapeake Bay, meat	0.03
3	Oyster, Chesapeake Bay, liquor	None
4	Oyster, Delaware Bay, meat	0.18
5	Oyster, Delaware Bay, liquor	0.01
6	Clam, Hardshell, meat	None
7	Clam, Hardshell, liquor	None
8	Crab, Soft Shell	None
9	Shrimp, Meat of Tails	None
10	Scallop, Muscle, Commercial Pack	None
11	Cocoa	0.53
12	Malt, 26 samples	0.11–0.15 Av. 0.13
13	Barley, 1 sample	0.07
14	Beer, American (3.2% alc.), 8 samples	Trace 0.02
15*	Milk, Fluid, Whole, 58 samples	0.14–0.19 Av. 0.16
16	Milk Powder, Whole, 4 samples	1.26–1.34 Av. 1.30
17	Milk Powder, Skim, 4 samples	1.78–1.85 Av. 1.82
18	Milk, Evaporated, Unsweetened, 3 samples	0.36
19†	Flour, Soft Winter Wheat	None
20	Flour, Hard Winter Wheat	None
21	Flour, Whole Wheat	0.05
22	Wheat, Bran	0.08
23	Wheat, Germ	0.34

†\* Items 15 to 18, inclusive, were published in *This Journal*, 16, 427 (1933).  
 Items 19 to 23, inclusive, *Ibid.*, 432.

grams of the ground material with water, cooling, diluting to 2 liters, and filtering through a large fluted filter paper.

In this investigation 29 fruits and 29 vegetables were examined for malic, citric, and tartaric acids. The tartaric acid results are not given because it is believed that the small quantities obtained are attributable to foreign acid-reacting substances in the cream of tartar precipitate. The indicated tartaric acid in the samples ranged from 0.004 to 0.014 per cent; only in the following instances was the maximum exceeded: Black raspberry, 0.028; quince, 0.018; artichoke, 0.020; avocado, 0.020; and grape juice, 1.07 per cent. A sample of dried commercial lentils showed a malic, citric, and tartaric acid content of 0.08, 0.39, and 0.19 per cent, respectively, and 1.11 per cent titratable acidity as citric.

The malic and citric acid results represent total acids, free and combined. Plants normally contain a portion of their acid content in combination with bases, so that the sum of the determined acids always ex-



ceeds the titratable acidity. Two fruits that show a titratable acidity in excess of the determined acids are the youngberry and the cranberry, this condition indicating the presence of comparatively large quantities of undetermined acids other than citric, malic, and tartaric acids. In the case of the youngberry the discrepancy is explained by the fact that this fruit is a cross between the loganberry and the blackberry, and the blackberry contains isocitric acid almost exclusively. The cranberry contains large quantities of benzoic acid and also quinic acid. In the case of the vegetables, 6 of the 29 samples showed titratable acidity in excess of the determined acidity, namely, artichoke, asparagus, beet, broccoli, mushroom, and the Cuban sweet potato. Without doubt an examination by the Franzen method would reveal the presence of substantial quantities of acids other than malic, citric, and tartaric.

Table 3 records the citric acid results obtained on 23 samples of miscellaneous food products. Items 1 to 9, inclusive, were prepared in the laboratory; the remaining samples were obtained in the market. The oysters and the clams were shucked, and the meats and the liquors were obtained by draining. The crabs were still alive when they were prepared; only the white meat was used. The shrimp tails were obtained from a fish dealer and were sound and fresh. Determinations of malic and tartaric acids of items 1 to 9, inclusive, gave negative results. The malts were obtained from breweries located in different parts of the country.

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## IMPORTANCE OF ENZYME ANALYSIS IN AGRICULTURAL CHEMISTRY\*

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In late years medicine and technology have commenced to utilize ferments for practical purposes. It is enough to call attention to the use of enzymic processes in such widely different fields as the drug industry, the tanning industry, and the textile industry.

At the same time the development of enzyme chemistry has helped the science of physiology—whether applied to plants or to animals—by furnishing a new series of chemical reactions which may be used to characterize physiological processes and conditions. Ordinary chemical analysis is often—too often—unable to do this. It is useless in answering such a question as whether a pile of plant seeds is alive or dead, and whether, if alive, the seeds are capable of sprouting. Many other qualities, of the greatest importance to the agriculturist, cannot be determined by chemi-

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cal analysis alone. The "baking-quality" of wheat, the "brewing-quality" of barley, and the "jelly-forming" quality of fruit pectin come under this head.

Recent research, however, seems to indicate that enzyme analysis is capable of solving such problems as these; in fact it has already solved some of them. But this type of research is only beginning, and it is for this reason that so much effort has been made by agronomists to work out methods for the measurement of enzyme reactions, and by these methods to arrive at a physiological characterization of agricultural products.

A few of the recent results will serve to illustrate this idea. In what follows, free use has been made of the literature, particularly that of Russian and American chemists who have been publishing recently along these lines.

A number of proofs exist that different varieties of plants (of the same species) may be differentiated by their enzyme content. Wheat that ripens late contains more peroxidase than wheat that ripens early. The early ripening varieties of oats can be distinguished from the late ripening varieties in an early stage of the plant's development. The amounts of catalase and of amylase measurable are larger in the early ripening sorts.<sup>1</sup> This seems quite natural, for the early ripening grain must build up its substance in a shorter time, and therefore its metabolism must be faster. The catalase content seems to be a good measure of metabolic activity and of what one may call vitality.<sup>2</sup>

The same connection between catalase and vitality has been found with barley. The most vital seeds contain most catalase. Moreover, they sprout first in the malting process,<sup>2</sup> so that the catalase content of barley indicates what its behavior will be on malting. Apparently for the same reason, in many kinds of plants, catalase<sup>3</sup> and amylase<sup>4</sup> activity parallels resistance to cold weather.

It also appears that fruits and seeds decrease in enzyme content very markedly after they are ripe. This is particularly true of the oxidative ferments.<sup>5</sup> If the climate is such that complete ripening does not occur, which is the case with wheat grown in the far North or on high mountains, the catalase content is correspondingly greater.<sup>6</sup> It is therefore easy to determine the geographical source of a wheat by its catalase content, and this some Russian investigators have done.<sup>7</sup> More important, however, is the possibility of demonstrating differences in the "ripeness" of the grain after other tests for this purpose have ceased to be significant. This difference in enzyme content appears to be carried over into the

<sup>1</sup> N. E. Prokopenko, *C. A.*, 22, 2765 (1928).

<sup>2</sup> K. Myrbäck and S. Myrbäck, *Wochschr. Brau.*, 49, 1 (1932).

<sup>3</sup> A. Okanenko, *C. A.*, 25, 5688 (1931).

<sup>4</sup> H. M. Tyedal, *J. Agr. Research*, 48, 219 (1934).

<sup>5</sup> A. Bach, A. Oparin, and R. Wähner, *Biochem. Z.*, 180, 363 (1927).

<sup>6</sup> N. Ivanov, *Biochem. Z.*, 254, 71 (1932).

<sup>7</sup> H. Lüers, H. Fink and W. Riede, *Wochschr. Brau.*, 47, 393 (1930).

flour, at least to some extent, in the case of barley, for the "oxidation-capacity" of the flour varies also with the "ripeness" of the grain, being greater in unripe meal.<sup>1</sup>

The same idea has been carried out with castor beans, the critical ferment being the lipase.<sup>1</sup> Beans from the North are not fully ripe; their lipase content is higher, and so are both the iodine value and the free acid value of the oil made from them.

The converse of this principle is also true. If placed under influences which artificially stimulate its enzymic activity, particularly its oxidative activity, the fruit ripens rapidly. Ethylene, as the Department of Agriculture has shown, exerts such an influence, and this is the basis for the ethylene treatment, which is now of such great importance to the citrus fruit industry.<sup>2</sup> The production of ferments by the plant cells appears to be stimulated, and if this stimulation is kept up too long the fruit not only ripens but autolyzes and decays rapidly.

These principles apply equally to animal material. According to a Swiss investigator, the catalase content of milk (and of blood and tissues too) varies inversely with the oxygen in the air.<sup>3</sup> Consequently milk from the mountains presents an enzymic picture very different from that of milk from the valleys. The activity of the proteolytic ferment in hens' eggs seems to vary with the age of the egg.<sup>4</sup> When an egg is about a day old its ferment content has fallen to a very low point. Later it comes up again; if the egg is incubated, through processes connected with growth, or if the egg is "stored," through processes connected with autolysis.

This form of agricultural research is new, and possesses, like most undeveloped ideas, its own inherent imperfections. For example, one may talk glibly about the "enzymic content" of a material. Except in one or two special cases nothing is known about the total amount of the enzyme present. What is measured is the active, or sometimes the activable, enzyme. If inhibited enzyme is there in addition, its presence will remain unknown until a way is found to render it active.

Nothing can be told about the amount of an enzyme present unless that enzyme is active or can be activated. Activators are known for some enzymes, but it is not improbable that there are many more that are still unknown. The conclusions just mentioned regarding catalase apply to the active enzyme. Yet catalase has an activator,<sup>5</sup> and the amount of inactive enzyme is often greater than that of the active. In this laboratory it was found that bacteria grown at high oxygen tensions contain less active catalase than when grown at low. They need less. But they contain relatively enormous amounts of inactive catalase. The bacteria do not

<sup>1</sup> N. Ivanov, *Loc. cit.*

<sup>2</sup> F. E. Denny, *Botan. Gaz.*, 77, 322 (1924); E. M. Chace and C. G. Church, *J. Ind. Eng. Chem.*, 19, 1136 (1927).

<sup>3</sup> A. Staffe, *Biochem. Z.*, 243, 390 (1931).

<sup>4</sup> A. K. Balls and T. L. Swenson, *Ind. Eng. Chem.*, 26, 570 (1934).

<sup>5</sup> A. K. Balls and W. S. Hale, *J. Am. Chem. Soc.*, 54, 2133 (1932).

need to make more catalase if they are placed in dilute air. They need only to activate part of their reserve supply.

The conclusions derived from such enzyme analyses are clear and definite. They serve to characterize the material in a way that chemical analysis can seldom do. In many instances, variations in the enzyme systems found in agricultural products can now be interpreted in terms of physiological condition. But an explanation of how these changes in ferment activity are brought about, in other words, a knowledge of what happens to the enzyme whose activity varies, would teach much more. It would explain what ripening and "ripeness" really are. It would tell whether the enzymes come and go in the cells, or whether they become alternately activated and inactivated by independent substances of another class, by hormones, for example. There are reasons which lead one to think that the latter explanation is the more probable.

It is impossible to leave this subject without first pointing out the limitless field which these studies have opened up. Those who are interested will readily see that there are three kinds of work to be done. First, the search for reliable methods of determining the ferments in agricultural materials. It is not so easy as it sounds. Second, a search for definite connections between the ferments present and the biological behavior of the material. Only a few of such accomplishments have been summarized; the greater part remains unknown. Third (and most difficult), a search whose object is to explain the connection—for there is one—between the biological behavior and the action of the enzyme.

When this third chapter is reasonably well worked out, the knowledge of the principles of agriculture so obtained will place agronomy among the exact sciences.

## NOTE ON DIFFERENTIATION BETWEEN LIGHT AND HEAVY MAGNESIUM OXIDE

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The Revision Committee of U.S.P. XI proposes the following test to distinguish between the light and heavy grades of magnesium oxide (Circulars, pp. 969-970).

Place 1 gm. of magnesium oxide, previously sifted through a No. 100 sieve, in a 50 cc. graduated cylinder provided with a glass stopper. . . . Add distilled water until a volume of 50 cc. is obtained. Agitate the mixture for exactly one minute and set it aside for sedimentation. Within fifteen minutes the column of magnesium oxide measures not less than 30 cc., in case of the light oxide and not more than 5 cc. in case of the heavy oxide.

This test was carried out on eight samples of magnesium oxide repre-

senting the grades supplied by three manufacturers. The results are given in the table.

MANUFACTURER	GRADE	SEDIMENT	APPARENT SPECIFIC GRAVITY		MICROSCOPIC EXAMINATION
			WITHOUT TAPPING	WITH TAPPING	
A	heavy	1 <sup>a</sup>	0.49	0.67	Large irregular fragments
A	light	48 <sup>b</sup>	0.10	0.25	Rods and needles
A	extra light	50	0.08	0.21	Very fine needles
B	light	20 <sup>c</sup>	0.10	0.24	Very fine needles
B	extra light	18 <sup>d</sup>	0.08	0.20	Very fine needles
C	heavy	2 <sup>e</sup>	0.61	1.05	Large irregular fragments
C	medium light	6.5 <sup>e</sup>	0.31	0.60	Very small spherical masses
C	extra light	50	0.07	0.19	Very fine needles

<sup>a</sup> 1 cc. heavy sediment; 2 cc. lighter sediment; whole column turbid.

<sup>b</sup> Upper 2 cc. of column clear.

<sup>c</sup> Upper layer slightly turbid.

<sup>d</sup> Upper layer very turbid.

<sup>e</sup> Upper liquid slightly turbid.

It is interesting to note that the extra light magnesium oxide obtained from Manufacturer B showed more sediment than did his light grade, although it was a much bulkier product. According to the proposed test these products are neither heavy nor light. Specific gravity measurements of all samples (range 2.9–3.2) showed no appreciable differences.

Deeney<sup>1</sup> found the apparent specific gravity of light magnesium oxide to be 0.122–0.128 and that of heavy oxide 0.447–0.474. He states that the cylinders containing his magnesium oxide were tapped gently. Liverseege, Bagnall and Lerrigo<sup>2</sup> placed 20 cc. of magnesium oxide in a cylinder of 18 mm. diameter and tapped sufficiently to level the powder. They report values of 0.08–0.15 for the light oxide and 0.36–0.39 for the heavy oxide. A similar test adopted by the Danish Pharmacopoeia<sup>3</sup> provides that after having been passed through a No. 10 sieve 250 cc. of magnesium oxide (light) shall weigh not more than 35 grams. This standard permits a maximum apparent specific gravity of 0.14 for light magnesium oxide.

The samples of magnesium oxide described were examined according to the methods suggested by both Liverseege and Deeney and also microscopically. The results are shown in the table.

It is apparent from these results that tapping the cylinder materially influences the results. To obtain concordant results any test of this type must be carefully standardized in regard to the size of the cylinder and the amount of tapping. The light magnesium oxides appear to consist of needles and rods. The heavy magnesium oxides consist of larger

<sup>1</sup> *Am. J. Pharm.*, 104, 22 (1932).

<sup>2</sup> *Pharm. J.*, 117, 146 (1926).

<sup>3</sup> *Pharmacopoea Danica*, p. 330 (1933).

massive fragments of irregular shape. One sample labeled "medium light" had a different appearance from either the light or heavy samples. In both the sedimentation test and the bulk-weight relationship, this specimen appeared much closer to the heavy oxides than to the light oxides.

#### SUMMARY AND CONCLUSIONS

The proposed U.S.P. XI sedimentation test can not be depended upon to distinguish between the light and heavy magnesium oxides. A weight-bulk relationship will distinguish between the two types, but it must be accurately standardized to give consistent results. It appears from the few samples examined that microscopic examination may prove to be the most promising means of differentiating the two types of oxide.

#### NOTE ON THE U.S.P. TEST FOR "SOLUBLE ALKALIES" AND ALKALINITY IN MILK OF MAGNESIA AND MAGNESIUM OXIDE

By H. WALES (U. S. Food and Drug Administration,  
Washington, D. C.)

United States Pharmacopoeia X provides the following test for milk of magnesia:

Dilute 20 cc. of Magnesia Magma with distilled water to make 200 cc. and allow it to stand until the precipitate has settled. . . . To a 50 cc. portion of the supernatant liquid, add 1 drop of methyl orange T.S. and titrate with tenth-normal sulphuric acid: not more than 0.4 cc. is required to produce a red color (soluble alkalies).

The Subcommittee on Analytical Assay Methods of the American Drug Manufacturers Association<sup>1</sup> claims that this test is too stringent and proposes that it be modified by filtering the diluted solution and by using phenolphthalein as the indicator for the titration. The Revision Committee for U.S.P. XI (Circulars, p. 615) now proposes that the diluted milk of magnesia be filtered and that methyl red be used as the indicator for the titration. The Revision Committee also proposes to use methyl red as the indicator in the assay of milk of magnesia, although it has proposed no change in the indicator (methyl orange) for the assay of magnesium oxide.

In order to ascertain the end point for the assay of milk of magnesia and magnesium oxide, solutions of magnesium sulfate and magnesium chloride containing slight excesses of acid were titrated potentiometrically with sodium hydroxide solution. As may be seen in Fig. I the end points in the titrations, which are characterized by sharp breaks in the curves,

<sup>1</sup> Am. Drug Mfgs. Assoc. Procs., 1931, p. 232.

lie between pH 4 and pH 8. Neither methyl orange (transition interval pH 3.1-4.4) nor phenolphthalein (transition interval pH 8.2-10.0) is a suitable indicator for this titration. Methyl red (transition interval pH 4.2-6.3) is suitable and should be used for the assay of both magnesium oxide and milk of magnesia.

The proposed U.S.P. XI method for the determination of "soluble alkalis" was carried out on eight samples of products labeled "milk of magnesia" purchased on the open market and on three preparations made in this laboratory by the hydration of different grades of magnesium oxide. In each case 100 cc. of the filtered solution was used in order to lessen any error in determining the volume of acid consumed. The course of the titration was followed by means of a potentiometer. Table 1 shows the results of these titrations. The end point is arbitrarily assumed to be at pH 5.0 as the first tinge of red resulting from the use of methyl red as the indicator is noticeable at this point. The number of cubic centimeters of 0.1 N acid consumed has been expressed on the basis of the 50 cc. sample specified by the Pharmacopoeia.

TABLE 1

SAMPLE	METHOD OF MANUFACTURE	0.1 N ACID TO
		BRING TO pH=5.0
		cc.
1	U.S.P.	0.31
2	U.S.P.	0.52
3	U.S.P.	0.25
4	U.S.P.	0.80
5	Hydration of MgO	0.28
6	Hydration of MgO	0.43
7	Hydration of MgO	0.72
8	Hydration of MgO	0.64
Lab. sample	Hydration of heavy oxide	0.35
Lab. sample	Hydration of light oxide	0.33
Lab. sample	Hydration of extra light oxide	0.34

The curves for Samples 2, 3, and 4 (Fig. 2) are characteristic of the types obtained.

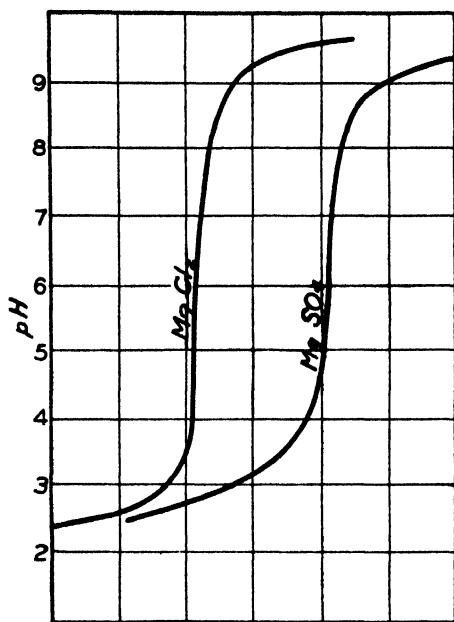
As indicated previously, with methyl red as the indicator all the magnesium hydroxide present, as well as other products more alkaline, will be titrated. All the curves indicate presence of carbonate by a change in slope at about pH 6.

According to Busch,<sup>1</sup> the solubility of magnesium hydroxide in water is  $2.14 \times 10^{-4}$  moles per liter; 50 cc. of a saturated solution would therefore require 0.21 cc. of 0.1 N acid for neutralization or half the quantity permitted in the "soluble alkalis" test. However, Busch points out that magnesium hydroxide is partially colloidal and that even when clear solu-

<sup>1</sup> *Z. anorg. allgem. Chem.*, 161, 161 (1927).



tions are used the apparent solubility of magnesium hydroxide will depend upon the fineness of the filter. The titration curves in Fig. 1 show that even at pH 9 the magnesium salts have not been completely converted to the hydroxide. Britton<sup>1</sup> has demonstrated that magnesium hydroxide will not precipitate until an alkalinity of pH 10.49 is reached. Any test for alkalis other than magnesium hydroxide, therefore must meas-



C.C. ALKALI ADDED →  
FIG. 1

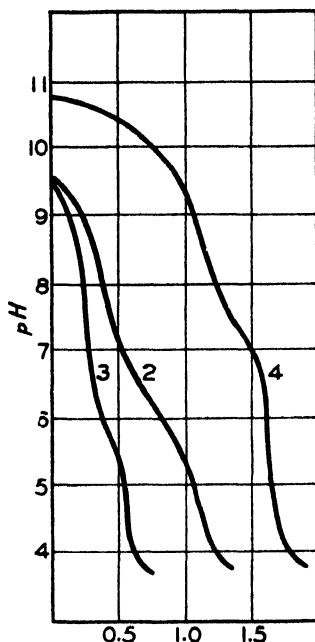


FIG. 2

ure only those products that are more alkaline than magnesium hydroxide, and some indicator having a color change above pH 10.5 must be used. The slopes of the upper ends of the titration curves (Fig. 2) indicate that if any such products are present the quantities must be negligible because the curves fall sharply to the neutralization point of magnesium hydroxide.

It has been suggested that the pH of the filtered solution as determined by nitramine (picrylmethylnitramine or 2, 4, 6 trinitrophenylnitramine) will serve to show the presence of foreign alkaline material in milk of magnesia and magnesium oxide. Very little information concerning this indicator was found in the literature. Kolthoff and Furman<sup>2</sup> give the transition interval (p. 71) as pH 10.8–13.0 and (p. 254) as pH 11.0–13.5.

<sup>1</sup> *J. Chem. Soc.*, 125, 2115 (1925). See also Hildebrand, *J. Am. Chem. Soc.*, 35, 867 (1917).

<sup>2</sup> Indicators. John Wiley & Sons, Inc. (1926).

As this indicator could not be found on the market it was prepared according to the method of Van Romberg.<sup>1</sup> When recrystallized from alcohol the product melted at 127°C. When tested in the borax-sodium hydroxide buffer mixture of Sørensen and the sodium carbonate-hydrochloric acid buffer mixtures of Kolthoff, and a concentration of 10 drops of indicator to 5 cc. of solution was used, the color changed from a yellow to a reddish brown, the first tinge of red appearing between *pH* 10.35 and *pH* 10.55. Kolthoff<sup>2</sup> states that a saturated solution of magnesium hydroxide has a weak alkaline reaction towards nitramine. From this statement and from

TABLE 2

MILK OF MAGNESIA		MAGNESIUM OXIDE		
SAMPLE (SEE TABLE 1)	<i>pH</i> OF SOLUTION	MANUFACTURER	GRADE	<i>pH</i> SOLUTION
1	11.1	A	heavy	10.3
2	10.4	A	medium light	10.1
3	10.1	A	extra light	10.3
4	12.5			
5	10.1	B	heavy	10.3
6	10.0	B	light	9.7
7	11.6	B	extra light	9.9
8	11.6			
Lab. sample	10.4	C	light	9.7
Lab. sample	10.0	C	extra light	9.5
Lab. sample	9.9			

Britton's work (*loc. cit.*), which shows the *pH* of such a solution to be 10.49, it is evident that this indicator is not suitable for the detection or determination of caustic alkali.

All the samples described in Table 1 were tested with nitramine, and their *pH* was determined electrolytically. Eight samples of magnesium oxide representing the various grades sold by three manufacturers were also tested by these methods. The results are shown in Table 2.

All samples showing a *pH* of 10.4 or higher gave a reddish brown color with nitramine. Comparison with Table 1 will show that the titration figure for Sample 1, *pH* 11.1, was 0.31 cc. of 0.1 *N* acid while that for Sample 2, *pH* 10.4, was 0.52 cc., showing that there is no connection between the *pH* of the solution and the titration for "soluble alkalies."

<sup>1</sup> *Rec. tran. chim.*, 2, 109 (1883).

<sup>2</sup> *Ibid.*, 41, 791 (1922).

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Index 1884-1929, Inclusive

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## FOREWORD

A careful survey of the activities of the Association and a review of its voluminous methods and proceedings showed conclusively that an index of the publications of the Association should be prepared. That much of the excellent work of the early days of the Association is not available to all the referees of the present day has been evident at times when new work was being planned. The proceedings and detailed reports of referees of the first few years appeared in pamphlets, and later in bulletins of the Bureau of Chemistry of the United States Department of Agriculture. Since 1913 the proceedings have been published in the *Journal of the Association*, and the methods have been issued in book form under the formal title, *Official and Tentative Methods of Analysis of the Association of Official Agricultural Chemists*, or the well-known shorter title, *Methods of Analysis, A.O.A.C.*

These and other reasons I brought to the attention of the Executive Committee at the Annual Meeting in 1931, suggested the preparation of the index, and presented an estimate of its cost. After a thorough discussion the Executive Committee approved a recommendation and appropriated the money for this purpose. Additional clerical help was secured, and the work was organized under the immediate direction of Miss Marian E. Lapp, the Assistant Secretary of the Association. Dr. C. A. Browne has given valuable consultation service regarding the arrangement and presentation of the data.

The preparation of the index has been a real task, as it covers all the publications of the Association from its organization in 1884 to 1929, inclusive, with one exception, that of Wiley's *Principles and Practice of Agricultural Analysis (Fertilizers and Insecticides)*. It is proposed to issue a supplementary index for 1930-1939, inclusive, and each ten years thereafter. This arrangement will synchronize the indexes with the revised editions of *Methods of Analysis, A.O.A.C.*

This index covers entries from—

(1) The proceedings of the Association published in *Bureau of Chemistry Bulletins* and indicated by the letter "B," followed by the number of the bulletin in bold-faced type, and this by the page number.

(2) The proceedings of the Association published in its *Journal* and indicated by the letter "J," followed by the volume number in bold-faced type, and this by the page number.

(3) The editions of *Methods of Analysis, A.O.A.C.* for 1920, 1925 and 1930, indicated by the letter "M," followed by the year in bold-faced type, and this by the page number.

This index is presented to the Association in the hope that it will fully meet a great need.

W. W. SKINNER  
Chairman, Editorial Board

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